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Author
Dariel, Moshe P.

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Moshe P. Dariel

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DIFFUSION IN RARE-EARTH METALS

Moshe P. Dariel†
Materials and Molecular Research Division
Lawrence Berkeley Laboratory
Berkeley, California

12.1. INTRODUCTION

Since the beginning of this century, the various aspects of diffusion in metallic systems have been extensively investigated. The considerable practical importance of diffusion-controlled processes in many fields of modern technology resulted in a large number of phenomenological studies. Investigations of mass transport in metallic lattices yield valuable information concerning the basic properties which determine the mobilities of atoms. Mass transport is affected to a large extent by the concentration and nature of the defects present in a metal. Diffusion studies offer an insight into the interaction between the atoms in a metal with various defects such as vacancies, interstitials and dislocations.

Contrary to the huge amount of experimental data available for many of the common metals, there is a relative paucity of information concerning the rare-earth metals. This situation is the result of several factors. The rare-earth metals or rare-earth rich alloys have found, up to quite recently, only limited use in technologically important processes. There was, therefore, no practical incentive

†On leave from the Department of Materials Engineering, Ben-Gurion University of the Negev and the Nuclear Research Center-Negev, Israel.
to carry out diffusion studies in these materials. As for the more basic type of research, the destructive nature of the experimental techniques and the relative scarceness of high purity single crystals, coupled with the usually high reactivity of the rare-earth metals at elevated temperatures were sufficient to discourage researchers from undertaking studies in these materials.

On the other hand, the rare-earth elements constitute about one fourth of all existing metals. They form a group of elements closely related in their chemical, physical and metallurgical properties. In particular, most rare-earth metals possess a similar electronic structure while other relevant properties often vary in a gradual, systematic manner. Thus, it appears that the rare-earth metals constitute, potentially at least, favorable systems for the study of some of the basic factors which determine diffusion mechanisms in metallic systems.

In retrospect, after several years of diffusion studies in rare-earth metals, these expectations seem to have been fulfilled. Several of the currently most interesting subjects related to diffusion in metals have been encountered in the course of these studies. Diffusion in rare-earth metals is an area far from being exhausted and further fruitful activity in this field of research can be expected.

The experimental techniques, with emphasis on their use in rare-earth metal systems, are briefly examined in §2 of this chapter. Self-diffusion in the close-packed and body-centered cubic structures is treated in §3. The current models, put forward to account for anomalous diffusion in bcc metals in general and the rare-earth
metals in particular, are also discussed in §3. The diffusion of metallic solutes in the rare-earth metals is reviewed in §4. Electrotransport studies, with emphasis on their relevance to diffusion, are summarized in §5. Finally, §6 is concerned with several diffusion related subjects, i.e. chemical diffusion (§6.1), diffusion of rare-earth solutes in non rare-earth metals (§6.2) and diffusion in rare-earth containing intermetallic compounds (§6.3)

12.2. EXPERIMENTAL TECHNIQUES

Experimental techniques using radioactive tracer methods are considered as being the most reliable and accurate for the determination of self or solute diffusion coefficients in metals (Tomizuka, 1959). The great majority of the diffusion studies in rare-earth metals has, indeed, been carried out using the thin layer sectioning or grinding of samples which had previously been coated by a surface layer of radioactive tracers. The details of this method and its variants, such as the residual activity measurement, have been described in many details (Adda and Philibert, 1966). In the following, mention will be made only of those points which are specific to diffusion studies involving the rare-earth metals. More detailed descriptions of the experimental details can be found in the original theses devoted to diffusion studies in rare-earth metals (Dariel, 1968; Languille, 1973; Zanghi, 1975; Fromont, 1975).

Purity of Samples - Most authors report a purity of 99.9 w% for the rare-earth metals used. It is believed that too often this figure represents an over optimistic estimate, in particular, when
rare-earth metals of commercial stock were employed. The light elements represent the bulk of impurities found in the rare-earth metals. These impurities, often hard to assess, are present at concentrations at least one order of magnitude higher than the non rare-earth metallic impurities. The solubility of the light elements in the rare-earth metals is, in general, very restricted and lower than their concentration. The light impurities react with the rare-earth matrix to form compounds which appear as inclusions under metallographic examination. No information on the effect these impurities have on diffusion processes in rare-earth metals is available, even though it might be significant in some instances.

**Single crystal versus polycrystalline samples.** In accurate diffusion experiments, the use of single crystals is highly recommended in order: 1. to eliminate the presence of short circuiting grain boundaries and, 2. to reveal any anisotropy effects in non-cubic crystals. Actually most of the available, highly reliable diffusion data on diffusion in most common metals has been derived from the studies of single crystal specimens. Unfortunately, even though single crystals are by now available for almost any of the rare-earth metals, they are expensive and difficult to grow. Considering the destructive nature of diffusion experiments, it is not surprising that few results in rare-earth metals have been obtained using single crystal samples.

**Chemical reactivity.** Most rare-earth metals oxidize readily and react with container materials at elevated temperatures. Also, the often employed method of depositing the thin radioactive
tracer layer by electrolytic coating from aqueous solution is unpracticable since it results in the formation of a surface oxide barrier layer. Usually vacuum evaporation of metallic tracers or electrolytic coating from non-aqueous organic solutions have been employed. Diffusion anneals at high temperatures require protection of the samples from exposure to reactive gases or container materials. This was achieved by wrapping the samples in thin tantalum foils and sealing them in evacuated or inert gas containing capsules. Protective atmosphere was also required in some instances during the sectioning stage of the samples in order to prevent oxidation or even ignition of the thin chips.

Electrotransport, solid state electrolysis or, in other words, the migration of impurities under the influence of an electrical field, has been studied in the rare-earth metals mainly for the purpose of finding a suitable method of purification. The common approach in these studies is to start with an initially homogeneous distribution of a particular impurity in the sample and pass a relatively high d.c. current through it. Under the influence of the electric field and as a result of momentum transfer between the charge carriers and the impurities, a concentration gradient of these impurities is set up. If the experiment is carried out for a sufficiently long time, steady state conditions are achieved. It can be shown (Verhoeven, 1966) that by analyzing the concentration profile of the impurities, relatively reliable diffusion coefficients can be deduced. Since a lengthy anneal at high temperature is required for setting up the steady state distribution, problems of
contamination from the surrounding atmosphere and the current carrying electrodes usually arise. Methods of overcoming these difficulties have been discussed by Jordon and Jones (1973) and Carlson et al. (1975). Electrotransport has been used mainly for the purification of the rare-earth metals from light, non-metallic impurities.

12.3. SELF-DIFFUSION IN RARE-EARTH METALS

12.3.1. Self-Diffusion in Close-Packed Structures

Most studies of self-diffusion in rare-earth elements have been motivated by the desire to clarify the problems involved in identifying basic diffusion mechanisms in metals. It is useful therefore, to begin this section by recalling the main features which are believed to be characteristic of a normal diffusion mechanism. These features can be summarized by several semi-empirical rules which have evolved as a result of studies in metals in which diffusion takes place by a vacancy mechanism. This is the reason for the present tendency to identify normal diffusion with a vacancy mechanism, in contrast to anomalous diffusion to be discussed later. The semi-empirical rules have been listed by Le Claire (1965) as follows:

1. The temperature dependence of the self-diffusion coefficients follows an Arrhenius-type relationship, i.e. $D = D_0 \exp(-Q/RT)$ where $D_0$, the pre-exponential term, and $Q$, the activation energy, are temperature independent.

2. The activation energy correlates to the melting temperature ($T_m$) or the latent heat of melting ($L_m$) within 20%, $Q = 34 T_m$ or $Q = 16.5 L_m$. 
3. The pre-exponential term $D_0$ is equal to unity within one order of magnitude

$$10^{-1} < D_0 < 10 \text{ cm}^2/\text{sec}$$

According to the Wert-Zener formulation, $D_0 = \gamma a_0^2 f \nu \exp(-\Delta S_v^v/R)$, where $\gamma$ is a geometrical factor, $f$, the correlation factor, $a_0$, the lattice parameter, $\nu$, a characteristic vibration frequency usually the Debye frequency and $\Delta S_v^v = \Delta S_f^v + \Delta S_m^v$ is the entropy associated with the formation and migration of the vacancy.

Theoretical calculations which have been borne out by the experimentally observed values of $D_0$ in regular fcc metals show that $\Delta S_f^v$ is positive for a vacancy controlled diffusion mechanism. The formation of a vacancy results in the lowering of the vibrational frequency in its neighborhood, implying a positive value for $\Delta S_f^v$. The motion of the atom through the saddle point configuration between lattice sites causes an increase of the local vibration frequency. This effect, however, is more than offset by the lowering of the overall frequency due to relaxation at the free surface (Vineyard, 1957). Thus, the entropy of migration for a vacancy $\Delta S_m^v$ is also positive and usually small. Positive values of $\Delta S_v^v$ account for the observed range of $D_0$ values associated with the vacancy mechanism. Recent accurate experimental work has shown that the first of the above-mentioned criteria is not being rigorously followed in fcc metals such as Ni or Au. The rather minor deviations from a linear Arrhenius-type behavior have been ascribed to the contribution or bi-vacancies to self-diffusion in the temperature
range $T > 0.8T_m$ (Seeger, 1972).

A variety of close-packed structures are observed in the rare-earth elements. Actually all rare-earth metals, with the exception of Eu, appear in at least one close-packed allotropic structure. Self-diffusion coefficients have been determined, however, in only a small fraction of the existing close-packed structures. The results are summarized in Table 12.1. Two widely divergent sets of results have been obtained in fcc $\beta$-La and hcp $\alpha$-Y. In $\beta$-La, the early results of Zamir and Schreiber (1964) were determined using an N.M.R. technique. The self-diffusion coefficients in $\beta$-La were later remeasured by Dariel et al. (1969b) who employed the more direct radioactive tracer method. Dariel et al. also pointed out the possible source of the discrepancy between the two sets of results. In Y, the more recent measurements of Gornyy and Al'tovskiy (1970), who used single crystals, seem more reliable than the older results by Maskalets et al. (1967). Considering only the more recent results in these two metals, it appears that in the close packed structures the pre-exponential terms and activation energies conform rather well to the semi-empirical rules mentioned above. Thus, since self-diffusion in the close packed rare-earth structures seems to follow in a satisfactory manner the criteria associated with a vacancy mechanism, there appears little reason to believe that it proceeds by a different mechanism. Further evidence for a vacancy controlled diffusion mechanism is based on some chemical diffusion experiments performed in the La-Ce system (Dariel, 1968). These results will be discussed in more detail in ch. 12 §6.1. Briefly, a Kirkendall shift of inert markers placed at the initial
interface of La-Ce diffusion couples and a pronounced porosity on the Ce side were observed. These effects can be accounted for on the basis of an indirect type of diffusion mechanism (vacancies or interstitialcies) and seem to eliminate direct interchange or pure interstitial as possible alternatives.

Akimov and Kraftmakher (1970), using heat capacity measurements, determined the enthalpy of formation $\Delta H_f$ (23 kcal/mole) of thermally activated defects in $\beta$-La. This value represents one-half of the experimentally measured activation energy for self-diffusion (Dariel et al., 1969b). Since $Q = \Delta H_f + \Delta H_m$ (with $\Delta H_m$ the enthalpy of migration of the defects) and since it is well established that $\Delta H_f \approx \Delta H_m$ for vacancies as diffusion determining defects in fcc metals, the heat capacity results seem to constitute further evidence for a vacancy dominated self-diffusion mechanism in the close-packed structures.

Obviously, this evidence in favor of a vacancy mechanism for self-diffusion in rare-earth metals is indirect and fragmentary at best. It will be shown in the next sections that serious consideration is given to other than a vacancy mechanism for self-diffusion in the bcc and some solute diffusion in both the bcc and the close-packed phases. Furthermore, preliminary results (Marbach, 1975) concerning the pressure dependence of the self-diffusion coefficients in fcc $\gamma$-Ce indicate a negative activation volume, $\frac{\Delta V}{V} = -0.17$ ($V$ = atomic volume of Ce). Negative volumes have also been reported in the bcc phases of some rare-earth metals (see ch. 12 §3.2) and constitute
important arguments against the vacancy mechanism. If indeed, the presence of a negative activation volume is a real feature of self-diffusion in \( \gamma \)-Ce, it would then appear that the situation in this metal in particular, and perhaps in other close-packed rare-earth metal phases as well, is not as clear and simple as we would like to believe. It seems, therefore, imperative that further work be done to confirm definitively the vacancy mechanism as the self-diffusion controlling mechanism in the close-packed structures. With the increased purity of the available rare-earth metals and the possibility of growing or obtaining single crystals, critical experiments such as the Simmons-Baluffi, isotope effect, positron annihilation and more detailed and careful Kirkendall effect measurements may become realizable.

Gornyy and Al'tovsky (1970), Spedding and Shiba (1972) determined the anisotropy of self-diffusion in single crystals of Y and Er, respectively. Self-diffusion in Y seems to be strongly anisotropic in contrast to the results in Er. Further work, particularly in the hcp phases of the heavy rare-earth metals, should elucidate this problem.

12.3.2. Self-Diffusion in BCC Rare-Earth Metals

The experimental data concerning self-diffusion in the bcc structure of the rare-earth metals is given in table 12.2. This table includes the values of the activation volumes deduced from measurements of the pressure dependence of the self-diffusion
coefficients. The values measured for self-diffusion in ε-Pu, an actinide metal, have been added since they form, together with results of δ-Ce, the basis of the activated interstitial model (ch. 12 §3.3). Values of the ratio \( Q/T_m \) (\( T_m = \) melting temperature) are also shown as a criterion of the normality of self-diffusion in that particular phase. The inverse temperature dependence of the self-diffusion coefficients of several rare-earth metals is shown in fig. 12.1. In 4 of these metals, measurements have been carried out both in the close-packed and in the bcc phases. A common feature repeating itself is the discontinuous increase of the self-diffusion coefficients by about 2 orders of magnitude at the temperature of the phase transformation. This point is of importance because, as shown in ch. 12 §4, the diffusivities of many solutes in the same matrices follow a different behavior. This discontinuous increase of the self-diffusion coefficients has been also observed in non rare-earth metals which undergo a close-packed to bcc phase transformation (Fe, Ti, Zr, Tl).

The initial motivation for the study of self-diffusion in the bcc phases of the rare-earth elements is connected to the problem of so-called anomalous diffusion in bcc metals. Any discussion of self-diffusion in the bcc rare-earth metals must be viewed with the background of this anomalous diffusion. This subject has received extensive coverage and has been summarized by Le Claire (1965), Lazarus (1965), Peterson (1968) and Seeger (1972).

Anomalous diffusion was first observed in β-Zr, β-Ti, β-Hf and γ-U. The main anomalous features which seem to characterize self-diffusion (and some solute diffusion) in these metals can
be summed up as follows.

1. A pronounced curvature of the Arrhenius plot is apparent whenever the temperature interval over which the measurements were made was wide enough to allow its detection.

2. The activation energy for the diffusion process (in the low temperature range for curved Arrhenius plots) is significantly lower than predicted on the basis of melting point or other semi-empirical correlations (fig. 12.2).

3. The pre-exponential term has values usually much lower than the \(10^{-1} - 10 \text{ cm}^2/\text{sec}\) range, leading actually to negative entropies of activation if a vacancy mechanism is assumed.

A survey in table 12.2 of the activation energies and the pre-exponential terms suggests that the bcc rare-earth elements, with the exception of Eu, are anomalous with respect to self-diffusion. Curved Arrhenius plots, even if present, could hardly be detected in view of the limited extension of the temperature interval over which the bcc phases exist. The anomaly appears to be of a variable degree, very pronounced for \(\delta\)-Ce and \(\beta\)-Gd, less so for \(\beta\)-Pr and \(\gamma\)-Yb. The low values of the activation energies, even though coupled with low pre-exponential factors, lead to very high self-diffusion coefficients as shown in fig. 12.3. These self-diffusion coefficients are among the highest observed in metals.

In the course of the past decade several explanations have been put forward to account for the anomalous diffusion in bcc metals. The different models based on the presence of extrinsic vacancies (Kidson, 1963), on the temperature dependence of elastic constants (Aaronson and Shewmon, 1967), on dislocation enhanced diffusion
(Peart and Askill, 1967) or on vacancy anharmonicity (Gilder and Lazarus, 1975) have been thoroughly discussed in the original and in the various review papers. Two additional models, the activated interstitial and, more recently, the ω-embryo model, have been proposed as alternative explanations for anomalous bcc diffusion. These two models and their possible common interpretation on the basis of the Engel-Brewer electron correlation theory will be discussed in the next sub-section.

12.3.3. The Activated Interstitial Model

The activated interstitial model has been put forward on the basis of self-diffusion measurements as functions of temperature and pressure in bcc ε-Pu and δ-Ce. These two metals possess certain unusual properties which set them apart of the other metals. Both Ce and Pu transform upon heating from the fcc to a bcc structure which subsists up to the melting point. In both metals, the melting is accompanied by an increase of density. This negative volume change is related through the Clapeyron relation, \( \frac{dT}{dp} = \frac{\Delta V}{\Delta S} \), to the negative slope of the liquidus in the respective p-T diagrams. Jayaraman (1965) suggested that the passage from bcc to liquid cerium involves a \( 4f \rightarrow 5d \) electron promotion and consequently a collapse of the atom to a smaller size. It is indeed well established from the study of lattice parameter relationships and magnetic properties that the energy level of the single \( 4f \) electron in Ce is close to the conduction band. This rather simple picture of Ce, based on the size consideration has not been borne out by
magnetic susceptibility measurement in the bcc and liquid phases (Burr and Ehar, 1966). The large scale promotion of electrons at the bcc-liquid transition was not confirmed and the slight decrease of the magnetic susceptibility could be accounted for by crystal field induced changes of the Pauli susceptibility. However, these experiments do not rule out altogether the possibility of electron promotion taking place in a small fraction of the Ce atoms. It also seems that in order to account for the negative volume change at melting in Ce, some kind of electronic transition which leads to the reduction of the ionic radius must be considered. The electronic structure of Pu is more complex than that of Ce, with several close-lying alternative electronic configurations, as witnessed by the numerous phase transitions occurring over a relatively narrow temperature interval.

Cornet (1971) having observed the negative activation volume in ε-Pu put forward the activated interstitial model, later extended by Languille et al. (1973) to Ce. According to this model a promotion of electrons takes place from the 5f to the 6d band in ε-Pu (4f and 5d in δ-Ce) on roughly 1% of the atoms. The atomic size of those atoms in which promotion takes place is reduced since, with the decreased screening by the f electrons, the outer d and s like electrons are drawn in by the nuclear change. The energy required for the formation of such a collapsed self-interstitial in an octahedral site is much lower than for an atom having undergone no electron promotion and could account for the low activation energies of self-diffusion. Furthermore, the formation volume of the activated interstitial, calculated using the elastic theory,
is negative and compatible with the experimentally observed values. Even though the negative activation volume does not rule out a vacancy mechanism, it does require for Pu a very large relaxation volume ($\frac{\Delta V}{V} \approx 0.67$).

Languille et al. (1974) tried to confirm the activated interstitial model by measuring self-diffusion coefficients in bcc $\gamma$-La, the first element in the lanthanide series. Simultaneous measurements were carried out by Dariel (1973) who also determined the solute diffusivity of La in bcc $\delta$-Ce. Both sets of measurements indicate that the general characteristics of self-diffusion in bcc $\gamma$-La are similar to those in bcc $\delta$-Ce (and $\epsilon$-Pu) with low activation energies and high diffusion coefficients (table 12.2). Languille et al. (1974) chose to interpret these results as confirming the $4f$ character in La metal, suggested on the basis of results concerning the pressure dependence of $T_c$ (superconductivity transition temperature), the compressibility at high pressures and the magnetic structure in some La-R alloys at low temperatures. However, even assuming that the $4f$ character of La subsists in the high temperature, normal pressure bcc phase, Languille et al. realized that the La matrix would still consist of a majority of atoms having a 2.7–2.8 valence and a minority undergoing electron promotion to valence +3, with a correspondingly small decrease of the atomic radius.

The activated interstitial model in its initial form did not appear, therefore, to be applicable to La and had to be modified. This was done as will be discussed below by Zanghi (1975).

Dariel (1973), on the basis of similar results, argued that it seemed highly implausible that the activated interstitial model
should yield similar results in bcc γ-La, δ-Ce and β-Pr considering
that the model depended so critically upon the number of 4f electrons
of the migrating atom and the possibility of their promotion to
the conduction band. According to Dariel, the common diffusion
behavior ensues from the particular properties of the bcc
structure of the rare-earth elements rather than from the electronic
structure of the various diffusing species.

In order to achieve a better understanding of anomalous bcc
diffusion behavior, Zanghi (1975) carried out a series of self-
diffusion measurements as function of pressure of Pu in stabilized
bcc Pu-Zr alloys. Zanghi also determined the solute diffusivities
of Am in these alloys as a function of temperature and pressure. The
results indicated that the activation volume of Pu increased from
its negative value in pure ε-Pu (table 12.2) to +0.2 atomic volume
at 40 at. % Zr. With respect to the diffusivities of Am, a quasi-
similarity was observed between the self-diffusion behavior of Pu
on one hand and the solute diffusivity of Am on the other. It thus
appeared, following the same arguments as those put forward by
Dariel (1973), that diffusion in these systems takes place by
means of defects having a volume and an energy of formation which
do not depend critically on the diffusion species.

On the basis of these results, Zanghi (1975) modified the
activated interstitial model by suggesting that the elementary
defect (initially a simple interstitial) was actually a many-body
defect with a self-interstitial at its core. Within the volume
of this many-body defect, compressive stresses are set up due to
the presence of the interstitial. These stresses, causing a reduction of the interatomic distances, favor an increased $d$-$f$ hybridization in the solvent atoms (Pu or Ce) through an enhanced overlap of their respective wave functions. Jullien et al. (1973) have shown that $d$-$f$ hybridization plays an important role in determining both the properties and the structure of the various Pu allotropes. The elastic energy involved in the formation of self-interstitials is high enough to prevent the formation of such defects under ordinary circumstances. In Pu, however, and, by extension, possibly in Ce, the elastic stresses can be alleviated by the possibility of some of the neighboring atoms to an interstitial to reduce their interatomic distances, by undergoing an electronic transition through increased $d$-$f$ hybridization. Thus, the elastic energy should be reduced, making the presence of a self-interstitial at the core of the many-body defect plausible.

With respect to the negative activation volumes (table 12.2), Zanghi used the elastic theory formula for the defect volume of formation $\Delta V^d_f$:

$$\Delta V^d_v = \Delta v \frac{\Gamma}{\Gamma_d} + \nu$$

where $\Delta v$ is the difference between the volume of the defect and the volume of the site in which the defect settles, and $\Gamma$ and $\Gamma_d$ are the Eshelby factors for the matrix and defect, respectively, with
\[ \Gamma = 1 + 4/3 \mu \chi_T = 3 \frac{1-\nu}{1+\nu} \]

\( \mu \), the shear modulus, \( \chi_T \), the isothermal compressibility and \( \nu \), Poisson's ratio.

The sign of \( V_{\text{at}} \), the atomic volume, depends on the nature of the defect, (+) for a vacancy, (-) for an interstitial. For the defect centered on the interstitial \( \Delta V > 0 \), but \( \Delta v_T / T_d < V_{\text{at}} \) will lead to negative values of \( V_f^d \). Thus, even if the activation volume is negative, an interstitial causes an expansion of the lattice in its immediate neighborhood \( (\Delta V > 0) \), favorable to the above mentioned \( d-f \) hybridization.

The modified activated interstitial model seems to account, qualitatively at least, for the low activation energies, negative volumes of activation and solute diffusion behavior in bcc \( \epsilon \)-Pu and possibly \( \delta \)-Ce. It also offers, again qualitatively only, an explanation for the low values of the pre-exponential terms which have been observed not only for \( \epsilon \)-Pu and \( \delta \)-Ce, but that are associated with all the anomalous bcc metals. It was shown in ch. 12 §3.1, that a vacancy mechanism through positive values of \( \Delta S \), the entropy associated with the diffusion process, accounts for the observed values of \( D_0 \) in normal metals. According to the modified activated interstitial model, the defect involved in the diffusion process comprises the interstitial and one or several surrounding shells of neighboring atoms. In the course of the formation of this defect with the interstitial at its core, compressive
stresses are set up which increase the vibrational lattice frequency and result in negative entropies of formation. The motion of a many-body defect might also be highly correlated, with low values of the correlation factor \( f \), leading to a further lowering of \( D_0 \).

12.3.4. The \( \omega \)-Embryo Model and the Engel-Brewer Correlation Theory

The activated interstitial model which hinges on the relative ease of some \( f \) electron promotion in its initial form or on the possibility of \( d-f \) hybridization in its modified form seems to account for the main anomalous features observed in connection with self-diffusion in bcc \( \varepsilon \)-Pu, \( \delta \)-Ce and possibly \( \gamma \)-La and \( \gamma \)-Yb. Beside these metals, however, anomalous diffusion has also been observed in \( \beta \)-Ti, \( \beta \)-Zr, \( \beta \)-Hf, \( \gamma \)-U and the rare-earth metals \( \beta \)-Pr, \( \beta \)-Nd and \( \beta \)-Gd. The normal behavior of Eu (table 12.2), which among this latter group of metals is the only one having the bcc structure as its only allotropic form, stands out in marked contrast to the other bcc rare-earth metals. It strongly supports Seeger's (1972) suggestion that anomalous diffusion in bcc metals is in some way connected to the phase transformation which precedes the bcc phase.

Recently Sanchez and de Fontaine (1975) suggested a new model in order to account for anomalous self-diffusion in Group IV-B metals, Ti, Zr and Hf. In these metals, beside the normal bcc to hcp transition, an alternative phase transformation takes place upon alloying or under pressure from the bcc to the metastable hexagonal \( \omega \) phase. Sanchez and de Fontaine pointed out that in bcc metals
the activated complex in the elementary diffusion process, that is the configuration with an atom in between two regular lattice sites, is actually identical with an \( \omega \)-phase embryo. In the neighborhood of the transition temperature from the bcc to the \( \omega \) phase, the free energy of formation of \( \omega \) will be small and, therefore, the formation of activated complexes will be greatly increased as compared to that in normal bcc metals. With increasing temperature, the thermal vibrations will tend to destroy the \( \omega \) embryos and diffusion will revert to a normal behavior. The presence of \( \omega \) embryos in the bcc phase has been confirmed by electron and neutron diffraction. A noteworthy feature of the \( \omega \) structure is the presence of some highly directional interatomic bonds. A detailed study of this structure led Doherty and Gibbons (1971) to postulate the simultaneous presence in the \( \omega \) structure of a pure IV-A element of two species of atoms with different electronic configurations. Thus, the \( \omega \) structure is stabilized by an electronic transition taking place in part of the atoms of the matrix. This picture is highly reminiscent of that postulated in the activated interstitial model, except that there are no \( f \) electrons involved.

Actually both models, the activated interstitial and the \( \omega \) embryo, can be viewed as special cases of a general diffusion behavior put forward by Engel (1965) on the basis of the Engel-Brewer correlation theory of metals. According to Engel, the presence of a phase transformation, whether to the \( \omega \) or to a
close packed phase, indicates that two (or possibly more) electron configurations have similar bonding energy (within terms of the order of $\Delta$S). Thus, when the difference in bonding energies corresponding to the two configurations is sufficiently small atoms having both electron configuration co-exist simultaneously. In other words, in a predominantly bcc matrix ($d^2$ configuration according to the Engel-Brewer theory, Brewer 1967), small clusters of atoms may momentarily possess an electron configuration and a spatial arrangement corresponding to a close-packed structure ($sp^2$ or $dsp$). In some special cases, the transition from one configuration to another may also involve change in the number of $f$ electrons, possibly accompanied by a change of the atomic radii. Such cases correspond to those considered in connection with the activated interstitial model. On the other hand, changes of electron configuration may, in principle, take place with no change in the number of $f$ electrons whenever there are none available (Ti, Zr) or when they are very stable (Hf, Pr, Nd and Gd). For these metals, the change of electron configuration would involve only a change in the relative number of $s$, $p$ or $d$ electrons. An estimate for the energy differences between the alternative electron configurations in non rare-earth metals was given by Engel (1965). Using the spectroscopic data reported by Brewer (1971), one can estimate the difference in bonding energies between the bcc and the hcp configuration in solid $\beta$-Pr and $\beta$-Gd to be of the order of 2kcal/mole. The distribution of the atoms in the 2 configurations and, therefore, the concentration of activated complexes will be
temperature dependent. This would lead to the curved Arrhenius plots observed in some of the anomalous bcc metals. Furthermore, the presence of clusters having a higher local density of atoms will certainly disturb severely the vibration spectrum of the matrix. It is not unlikely that it might actually increase the local vibration frequency leading to negative entropies of defect formation and, hence, to the low values observed for the pre-exponential factors.

The nature of the defect involved in the diffusion process is not specified at this stage. It would appear, however, that it is an extended, many-body defect. It might be a vacancy adjacent to an ω embryo, a strongly relaxed vacancy with reaccommodated nearest and next to nearest neighbors or a cluster of atoms with an interstitial at its core. The common feature of these extended defects would be, according to the Engel theory, their formation as a result of the availability of suitable, alternative electronic configurations for the matrix atoms.

12.4. METALLIC SOLUTE DIFFUSION IN RARE-EARTH METALS

This section is concerned with diffusion studies of metallic solutes at infinite dilution in rare-earth metals. Many such studies have been carried out in the more common metals, providing important insight into the fundamental details of the diffusion processes. About one decade ago the vacancy mechanism seemed firmly established as the dominant diffusion mechanism for self-diffusion and for diffusion of substitutional solutes in metals.
In a number of specific metal matrices (noble and some bivalent metals), successful quantitative models were developed to account for the relative values of solute diffusivities in a particular solvent. An electrostatic Coulomb interaction was assumed to determine the binding between the excess charge on the solute and the vacancies. Since the excess charge is generally well screened by the conduction electrons, the solute-vacancy binding energies are small with respect to the vacancy formation energy. This conclusion is especially valid for polyvalent solvent metals (e.g. the rare-earth matrices) where computations (March and Murray, 1961) have shown that the electron density surrounding an impurity charge is so high that the charge is screened at distances less than an atomic radius. It is not surprising, therefore, that the diffusivities of metallic solutes were observed to lie within one order of magnitude of the self-diffusion coefficients of the solvent matrices. Alternative diffusion mechanisms to the vacancy mechanism and, in particular, the interstitial one were not seriously considered because they implied the momentary occupancy, at least, of interstitial sites by metallic solutes. Since the ratio $r_A/r_B$ of the Goldschmidt radii of the components in metallic systems significantly exceeds the Hagg (1929, 1930) limit for interstitial solubility, $(r_A/r_B=0.59)$, such solutions seemed precluded on the basis of size considerations.

In the course of the past years, a growing body of evidence has shown that, with respect to the solute diffusion of metallic solutes, the situation is more complex than it would appear from the foregoing discussion. This conclusion is mainly based on the
increasingly numerous metallic systems in which the solute diffusivities were observed to exceed by several orders of magnitude the self-diffusion coefficients of the solvent metals. This behavior, called fast or ultra-fast diffusion, was first observed in Group IV-B (Si, Ge, Sn, Pb) and Group III-B (In, Tl) solvent metals. At present it is well established that fast diffusion also occurs in the alkali metals (Li, Na, K), the Group IV-A metals (Ti, Zr), the rare-earth metals and some actinides. Fast diffusion solutes are the noble metals (Cu, Ag, Au) and some transition metals (Fe, Co, Ni) and to a lesser extent Zn and Cd. Fast diffusion and its characteristic features have been reviewed by Anthony (1970) and Warburton and Turnbull (1975).

At present, fast diffusion is interpreted as taking place by a mechanism different from the vacancy mechanism which determines self-diffusion in metals (except possibly some bcc phases). This mechanism, as will be discussed below, implies the partial solubility of the fast diffusing solutes in interstitial sites of the solvent matrices. Since the great majority of the experimental results on solute diffusion in rare-earth metals reflects the fast diffusion behavior, the rest of this section will be mainly devoted to this subject.

The results of metallic solute diffusion studies in rare-earth metals are shown in table 12.3. Also included in this table are values of the ratio \( \frac{K_{A}^{B}}{D_{A}^{A}} = \frac{D_{A}^{B}}{D_{A}^{A}} \) (where \( D_{A}^{B} \) is the solute diffusivity of B in A and \( D_{A}^{A} \) is the self-diffusion coefficient of A), at the highest temperature at which it could be determined in each phase.
Most solute diffusion measurements have been carried out in Ce and Pr. The temperature dependence of the solute diffusivities in these two metals is shown in figs. 12.4 and 12.5.

As mentioned above, high values of $K_A^B$ are characteristic of the new interstitial-like diffusion of metallic solutes. Table 12.3 shows that these values of $K_A^B$ vary in a quasi continuous manner from $K_A^B \approx 1$ to $K_A^B = 2 \times 10^6$. Such an extended, continuous range for $K_A^B$ has also been observed in other metals such as Ti, U or Pb. Solutes having values of $K_A^B > 10^2$ seem to be fast solutes, diffusing by a mechanism different from that for self-diffusion. On the other hand, solutes with $K_A^B < 10$, probably diffuse by a mechanism similar to that for self-diffusion. This last group includes the rare-earth solutes and possibly non-transition metal polyvalent solutes (e.g. In).

The light rare-earth metals undergo a high temperature phase transformation from a close packed to the bcc structure. The self-diffusion coefficients increase by approximately two orders of magnitude upon change of the crystal structure (fig. 12.1). The slow diffusing solutes behave in a similar manner, strengthening the assumption of identical mechanisms in both cases. The effect of the phase transformation on the solute diffusivities provides the means of determining whether the solutes with $10 < K_A^B < 10^2$ are real interstitial fast diffusers or substitutional solutes diffusing by a vacancy mechanism at unusually high rates.
Anthony (1970) and Dariel et al. (1968) have pointed out that one of the characteristic and yet unexplained features of fast diffusion is the small, sometimes barely discernable effect exerted by the phase transformation taking place in the solvent matrix on the solute diffusivities. Such a behavior is in marked contrast to the discontinuous increase of the self and, presumably substitutional, solute diffusivities. Thus, using the effect of the phase transformation as a criterion, it appears that the noble metals, the transition metals (Mn, Fe, Co) and Zn behave as fast diffusers in the rare-earth metals.

Diffusion theory in metals, at its present state of art, is not able to provide a quantitative or even qualitative account for the relative values of the solute diffusivities in rare-earth metals. The electrostatic interaction theory, which achieved notable success is accounting for the relative diffusivities of various solutes in the noble metals is not applicable to the polyvalent rare-earth solvents (Dariel, 1968). Size effects are probably important in determining relative solute diffusivities. The available experimental data (Dariel et al., 1969a; Dariel, 1973; Fromont, 1975) does not yield, however, a consistent picture and more work is required on these systems.

With respect to the fast diffusing noble metal solutes, the trend $D_{Cu} > D_{Au} > D_{Ag}$ is similar to that observed in other matrices (Li, In, Tl, Sn, Pb). Noteworthy are the diffusivities of the transition metal solutes (Fe, Co) in the bcc phases of Ce, Pr and Nd (figs. 12.4 and
12.5). The measured values $3 \times 10^{-5}$ cm$^2$/sec are the highest measured for metallic solutes in crystalline matrices and are of the same order as the diffusivities in liquid metals. Indeed, the highest diffusivities in metals seem to be associated with fast solutes in anomalous bcc solvent metals. The giant diffusivities of transition metal solutes, higher than those of the noble metals, seem to be a feature common to Group III-A (rare-earth) and IV-A (Ti, Zr) metals, contrary to III-B and IV-B solvents in which noble metals have the highest diffusivities.

In a recent review, Warburton and Turnbull (1975) discussed the mechanism by means of which the fast diffusion of metallic solutes is assumed to take place. There seems to be general agreement that part or all of the fast diffusing solutes enter into interstitial sites during the diffusion process. Several independent experimental techniques, beside diffusivity measurements, have indeed confirmed that interstitial solubility, to a variable extent, occurs in these systems. Initially, Frank and Turnbull (1965) put forward the dissociative mechanism, according to which the measured diffusivity $D_m$ can be expressed by

$$D_m = \frac{C_i}{C_i + C_s} D_i + \frac{C_s}{C_i + C_s} D_s$$

where $D_i$ and $D_s$ are the diffusivities, $C_i$ and $C_s$ the concentrations of the solute in interstitial and substitutional positions, respectively. Postulating, for reasons at that time not yet clear, that $C_i$ is significantly larger than in usual metallic solid
solutions and assuming that the barriers for interstitial solute
motion are not too high, a qualitative explanation for the high
values of \( D_m \) can be found. Variations of the values of \( C_i \), \( C_s \),
\( D_i \) and \( D_s \) in the different crystalline structures can account for
any, including the slight positive or negative, solute diffusivity
discontinuities observed at the temperature of the phase
transformations of the solvent metals. However, the dissociative
mechanism, assuming a simple interstitial defect, is not consistent
with the results of isotope effect, solvent diffusion enhancement,
solute diffusion dehancement and internal friction results. More
complex defects such as associated interstitial-vacancy pairs,
solute-solute or solute-solvent split interstitials have been
proposed.

It is likely indeed, considering the great variety of metallic
systems in which fast diffusion has been observed, as well as the
extended range for \( K^B_A \), that several kinds of defects (ranging from
a pure interstitial to a simple vacancy) are involved in the solute
diffusion processes in the various systems.

The exceedingly high diffusivity of some metallic solutes in
the rare-earth elements suggests that a significant fraction of
these solutes is able to dissolve as interstitials. This is related
to the "open" structure of the rare-earth host atoms which possess
a relatively large ratio of the Goldschmidt to ionic radius. This
feature, coupled with the relatively small Goldschmidt radii of
the solutes, is a necessary (albeit not sufficient) condition for
the occurrence of fast diffusion.
The ratio of the Goldschmidt radii of the solute to that of the solvent atoms ranges from 0.7 to 0.9 in the fast diffusing solutes systems. These values greatly exceed the well-known Hagg limits for interstitial solid solution formation. The presence of a significant fraction of the solutes apparently violating these rules offers intriguing implications concerning the validity of the established laws for alloy formation. Size effects are undoubtedly important, but in a more subtle manner than previously believed. Turnbull (1974) pointed out that many binary metallic systems in which fast diffusion of one of the components was observed also show a tendency towards amorphous alloy formation when cooled from the liquid phase. This feature is well apparent in rare-earth metal solvent systems. Both rare-earth noble metal systems (Johnson et al., 1975) and rare-earth transition metal systems (Rhyne et al., 1972, Heiman and Lee, 1974) have a tendency for extensive amorphous solution formation and (table 12.3) for fast diffusion. Turnbull associates both features with the presence of a pair potential \( \phi_{AB} \) (A-solvent, B-solute) which has an abnormally soft repulsive branch. This accounts for these systems being relatively insensitive to the solute-solvent interatomic distance. As a result, solutes are able to approach solvent atoms without great expanditure of energy to within distances significantly smaller than the sum of the atomic radii of the pure elements. This model is supported both by theoretical calculations in alkali metals (Schober et al., 1974) and by experimental evidence reviewed by Turnbull (1974).
Undoubtedly the rare-earth metals, with the continuous change of size within the series, offer a highly promising field of study for these new, partly interstitial solid solutions. Examples of the variety of defect structures that can be obtained are the Y(Cu) and the Gd(Cu, Fe) systems. In the former, splat quenching (Giessen et al. 1971) yielded a purely interstitial solid solution; in the later, (Ray, et al. 1972) the solutes were in the form of bi-substitutionals i.e. associated solute pair at one lattice site.

Solute diffusion measurements have so far been restricted to Y and light lanthanide solvent metals; it seems highly desirable to extend such measurements to heavy lanthanide matrices. In particular, with the increasing availability of single crystals, efforts should be made to determine the anisotropy of solute diffusion in the hexagonal close-packed phases. Similar experiments (Dyson et al., 1967) provided useful evidence concerning the nature of fast diffusion.

In general the solubility of the fast solutes is severely limited in the solvent metals. By studying the solute concentration dependence of the solvent and the solute diffusivities, Miller (1969a, 1969b) and Warburton (1973), respectively, were able to draw important conclusions concerning the mechanism of fast diffusion. No such studies have yet been carried out in the rare-earth metals, even though in some instances (Pr(Au), Griffin and Gschneidner, 1971) the solubility of the fast diffusing solutes seems surprisingly large.

The amorphous solid solutions of the fast diffusing solutes in rare-earth metals possess some very interesting (superconductive,
magnetic) properties. This should provide a strong motivation for intensive studies of these systems. It is hoped that the increasing understanding of the structure and properties of amorphous solutions will yield additional insight into the nature of fast diffusion.

12.5. ELECTROTRANSPORT IN RARE-EARTH METALS

The presence of an external electric field induces an effect of mass transport in solids. If the temperature is sufficiently high, the atoms migrate either toward the anode or the cathode. The study of this effect, which has been alternatively called electromigration, electrotransport or electrorefining, has interesting aspects, both practical and theoretical. The main practical importance of electromigration lies in it being a potential method of purification. The electric field and currents cause the impurities to be driven toward one of the electrodes. Their accumulation at the edges leaves the sample with a decreased impurity content over most of its length. From the basic science point of view, electromigration experiments yield insight into the interaction between the migrating ion with the electric field and the charge carriers. The results of such experiments can be used to analyze solute diffusion kinetics and to deduce information on various vacancy jump frequencies. The experimental and theoretical aspects of electromigration and electrorefining have been reviewed extensively, the most recent reviews are those of Huntington (1975a, 1975b).
The highly reactive rare-earth metals show a strong affinity toward the non-metallic interstitial solutes i.e. carbon, nitrogen and oxygen. The concentration of these impurities is, therefore, usually high even in carefully prepared materials. Early experiments by Williams and Huffine (1961) and Marchant et al. (1961) had shown electrotransport to be a promising method of purification of the rare-earth metals, not only from non-metallic, but from some metallic impurities as well. These results provided the motivation for the overwhelming majority of electrotransport experiments which have been carried out in the rare-earth metals. The avowed objective of these experiments has been to study and optimize the parameters involved in electrorefining the various rare-earth metals. The experimental aspects of these studies in metals have been discussed by Peterson (1971), the use of this method for purification has been reviewed by Carlson et al. (1975) and is also treated in ch. 2. As a by-product of the electrotransport studies, valuable information concerning basic diffusion behavior in rare-earth metals could be deduced.

A variety of solutes in the rare-earth metals present a partly or total interstitial character. These solutes include beside the metalloid classical interstitials also some metallic elements, the so-called fast-diffusers, discussed in ch. 12 §4. In general the study of electromigration of interstitials offers two advantages as compared to that of substitutional solutes. From the experimental point of view, the relatively high mobilities of the interstitial solutes increases the electrotransport effects
often allowing to achieve steady state conditions within reasonable periods of time. From the theoretical side, the effects associated with interstitial diffusion are more readily interpretable. The defect structure of an interstitial is simpler than that of a vacancy and its scattering power stays constant during the diffusion process. Considering the relative variety of interstitials encountered in rare-earth metals, electrotransport studies present certain advantages which are, however, counterbalanced by having to work with high reactivity metals possessing complex band structures.

The main qualitative result of the electrotransport studies in rare-earth metals, namely the direction in which the various solutes are driven by the electric field and current, is shown in table 12.4. Quantitative results such as solute mobilities and diffusivities which in some instances could be deduced from the electrotransport data are shown in table 12.5. This table also includes some results deduced from internal friction studies of C, N and O in Y.

A survey of table 12.4 allows to draw certain general conclusions. The interstitial non-metallic solutes, C, N and O migrate in all instances toward the anode. In that respect, the rare-earth metal matrices are similar to Group IV-A (Ti, Zr) metals and different from the other transition metal solvents. The fast diffusing metallic solutes, discussed in §4 can be divided in two groups. The first group includes the ferrous transition metals Mn, Fe, Co and Ni. These solutes, like the metalloids, possess extremely high mobilities and diffuse toward the anode. The second group of fast diffusing solutes, the noble metals (Cu and Ag)
migrate toward the cathode. Whether this implies that Au would behave similarly, is not clear. In Pb (another matrix for fast diffusion), Ag diffuses toward the cathode while Au diffuses toward the anode (Herzig and Stracke, 1975).

According to all current electrotransport theories the force on a migrating ion in the electrotransport process consists of two parts. The first one represents the direct electrostatic interaction of the applied electric field with the migrating ion. The second force arises from the momentum transfer from the charge carriers scattered by the ion. This latter force will be anode directed in an electron conduction type metal and cathode-directed in hole conduction. The negative effective charge of the anode directed metalloids in Group III-A and IV-A metal matrices has been interpreted as indicating that the dominant electrotransport-determining effect is the momentum transfer term. In the elements lying to the right of Group VI-A, the reversal of the sign of the effective charge is then attributed to the influence of holes which become the charge carriers in the nearly filled high density bands. Unfortunately, this rather simplistic picture breaks down considering that the ferrous interstitial solutes behave like the metalloids but the noble metal interstitials show an opposite behavior. Undoubtedly the situation is more complex in the rare-earth metals which have several overlapping bands. The results indicate that the sign of the effective charge depends both on the nature of the migrating solute ion and that of the solvent matrix. Murphy et al. (1975) remarked that average properties such as the Hall effect
have only limited value in predicting the direction of electrotransport, as shown by the fact that Fe and Ag behave in a similar manner in Y and Ce, yet the Hall coefficient on Y is negative and that of γ-Ce positive.

Almost no results concerning the electrotransport of substitutional solutes in rare-earth metals have been reported. Even for interstitial solutes the results are fragmentary and mostly qualitative. Much is therefore to be yet done in order to achieve a coherent picture of electrotransport phenomena in rare-earth metals. The double challenge being offered by the practical applicability of such studies on one hand, and their importance towards furthering the understanding of basic diffusion phenomena in metals on the other, should provide the necessary motivation for additional research in this area.

12.6. VARIOUS DIFFUSION RELATED SUBJECTS

6.1. Chemical Diffusion Studies

The previous sections were concerned with self-diffusion or solute diffusion studies in which the environment of the migrating atoms did not change either as function of time or the spatial coordinates. In solute diffusion or electrotransport experiments these conditions were fulfilled as a result of the extremely low concentration of the diffusion species. Even if the distribution of the solutes changed as a consequence of the diffusion process, it did not affect in any significant manner the overall local composition
of the sample.

In chemical diffusion experiments, on the other hand, steep concentration gradients are set up which vary appreciably both as function of time and distance. As a result of the continuous varying environment in the diffusion zone, the interpretation of the results is much more complex. Chemical diffusion studies present, however, a practical interest since in many cases situations arise which involve the initial presence of concentration gradients.

The study of diffusion in systems with a concentration gradient allows the determination of $\tilde{D}$, the chemical diffusion coefficient, which in a binary system can be expressed as

$$\tilde{D} = (D_A^* N_B + D_B^* N_A)(1 + \partial^2 n \gamma_A / \partial^2 n_A)$$

where $D_A^*$, $D_B^*$ are the composition dependent intrinsic diffusivities, $N_A$, $N_B$ are the mole fractions of components A and B and $\gamma_A$, the activity coefficient of A. The second right hand term takes account of the deviations of the system from an ideal solution. A second equation relates the rate of displacement $v_k$ of inert markers placed at the initial interface of the diffusion couple to the intrinsic diffusivities.
The displacement of the inert markers and the micrographic aspect of the diffusion zone allows to draw some conclusions concerning the nature of the diffusion mechanism.

Dariel (1968) and Languille (1973) carried out chemical diffusion studies in La-Ce, Pr-Nd and La-Pr diffusion couples. The components of these systems are closely related in their properties, departures from an ideal behavior are therefore expected to be slight, as indeed was established in the Pr-Nd system (Lundin et al., 1965).

A significant shift of the inert markers and the formation of porosity were observed only in the La-Ce couples. The lack of inert markers shift in the other systems was attributed to the essentially similar intrinsic diffusivities of the two components. The concentration dependence of the intrinsic diffusivities (at constant temperature) seemed to correlate with the temperature of the solidus in the binary system. In all instances precipitates containing a ternary component, most likely oxygen, appeared in the diffusion zone, their presence was attributed to the difference in the solubility of oxygen in the two components of the diffusion couple.

Chemical diffusion-like studies were carried out in Pu-Ce δ stabilized bcc alloys (Harvey et al., 1968). The similarity between Pu and Ce was mentioned in §3.3. It is not surprising
therefore that Ce dissolves in and stabilizes δ-Pu.

6.2. Diffusion of Rare-Earth Solutes in Other Metals

Several investigations of the diffusion of rare-earth metal solutes in non rare-earth metals have been reported in literature (table 12.6). The main objective of these experiments has been the study of the diffusion behavior in a common solvent metal of a closely related group of solutes in which properties varied in a gradual and systematic manner. In particular, the results were expected to provide information concerning the validity of Swalin's (1957) treatment of solute diffusion in metals according to which mechanical properties such as size and deformability determine relative solute diffusivities.

In general, the studies showed a highly anomalous, structure sensitive diffusion behavior of the rare-earth tracers. Non-Gaussian penetration plots which usually consisted of an initial steep slope followed by a gradual decrease of the tracer activity were observed. These results were attributed to the overall low solubility of the rare-earth solutes in the metals (Al, Cu, Ni, Ag and Pb) examined, to the contribution of short-circuiting diffusion paths or to the presence of surface oxide barriers. Efforts were made to analyze the penetration plots in terms of contributions from several overlapping thermally activated mechanisms. As a consequence of the experimental difficulties and the ambiguity of the results, no conclusions could be reached concerning the
validity of Swalin's theory.

The solute diffusivity of Y in single crystals on several refractory metals was studied by Gornyy and Al'tovskiy (1971). A normal diffusion behavior has been reported with the activation energy of the solute diffusivity low as compared to that of the self-diffusion of the host metal.

A general conclusion of these investigations seems to be that the study of diffusion of rare-earth solutes in different metals has been less fruitful than diffusion studies carried out in rare-earth matrices.

6.3. Diffusion in Rare-Earth Containing Compounds

This last sub-section summarizes some diffusion related effects in compounds and especially in the SmCo$_5$-type compounds, which are probably the best known rare-earth containing intermetallics. These materials owe their usefulness to their outstanding magnetic properties and, in particular, to their exceedingly high magnetic energy product. SmCo$_5$-based permanent magnets have reached the stage of commercial production for a variety of applications. The properties and details of the preparation methods have been fully described in literature and are discussed in ch. 14.

SmCo$_5$-type magnets are prepared by a sequence of arc-melting, milling, magnetic aligning, compression and sintering steps. The relevant magnetic properties depend critically on the various stages. The mechanism of sintering and its relation to the intrinsic
coercive force has been studied by Benz and Martin (1972) who observed a 1/2 power dependence of the volume shrinkage of SmCo$_5$ pressings on the sintering time. These findings were later confirmed by Jorgensen and Bartlett (1975) and were interpreted, according to the prevalent theories of sintering, as suggesting grain boundary diffusion as the rate limiting step for the sintering process. Benz and Martin also studied the concentration dependence of the rate of shrinkage in the homogeneity range of the SmCo$_5$ phase. The highest rate of shrinkage was observed for hyperstoichiometric (Sm-rich) SmCo$_5$ compounds and attributed to the presence of structural Co vacancies on the Co sublattice. On the basis of these results Benz and Martin proposed a sintering model which includes a Co-vacancy flow from the curved surface of the pores toward the relatively planar grain boundaries which act as vacancy sinks. There is a net counterflow of Co and Sm atoms to the vacancy flux. The Co atoms are assumed to diffuse by direct interchange with the Co vacancies i.e. vacancies on the Co sub-lattice, whilst Sm atoms diffuse by a Sm atom-Co vacancy cluster interchange. The net flux of vacancies from the pore area and the counterflux of atoms result in the shrinkage and final annihilation of the pores. The rate-limiting step in this model is the diffusion of Sm atoms from the grain-boundary regions towards the pore surfaces.

The model, just described, depends on the observed concentration dependence of the rate of shrinkage with its maximum at high Sm-concentrations. These results have not been confirmed by Jorgensen
and Bartlett (1975), who suggest the presence of more than one (unspecified) transport mechanisms taking place most likely, along grain boundaries.

The mechanism of sintering in Sm-Co alloys has also been studied over a wide (23 to 42 w%Sm) composition range by Gessinger and de Lamotte (1973). These authors observed that the stoichiometric compounds Sm$_2$Co$_7$, SmCo$_5$ and Sm$_2$Co$_{17}$ are characterized by a relatively slow sintering behavior, while non-stoichiometric SmCo$_5$ shows maximum densification at the limits of its homogeneity range. These results were interpreted as being due to the effect of structural vacancies on the Sm and Co sub-lattices in the non-stoichiometric compound.

Beside their obvious contribution to sintering, diffusion processes are also important in determining the thermal stability of SmCo$_5$ type materials. The thermal stability and its influence upon magnetic properties is affected by 1. The eutectoid decomposition which takes place at elevated temperatures (Den Broeder and Buschow, 1972, Buschow and Den Broeder 1973); 2. the presence of oxygen. The eutectoid transformation is clearly a diffusion controlled process and its kinetics determine the stability of the SmCo$_5$-phases at low temperatures. Its presence in RCo$_5$ compounds has been definitively established by means of diffusion couple techniques in the Sm-Co (Martin and Smeggil, 1974) and the Ce-Co (Martin et al., 1973) systems.
The microstructural changes caused by the presence of oxygen and its diffusion during the sinter-annealing and the thermal aging stages have been studied by Bartlett and Jorgensen (1974). The selective oxidation of samarium sets up samarium activity gradients which may result in the apparition of samarium deplated phases. The mobility of oxygen may be beneficial since it allows the removal of oxide inclusions which coalesce in a few coarse grains.

All these processes may affect in a significant manner the magnetic properties (Searle and Garret, 1974) and, therefore, deserve further detailed studies.
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Table 12.1

Diffusion Parameters in Close-Packed Structures of Rare-Earth Metals

<table>
<thead>
<tr>
<th>Element</th>
<th>Structure</th>
<th>$D_0$ (cm$^2$/sec)</th>
<th>Q (kcal/mole)</th>
<th>$Q/T_m$</th>
<th>Temperature Interval (K)</th>
<th>Ref.</th>
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<tbody>
<tr>
<td>Y $\parallel^a$</td>
<td>hcp</td>
<td>0.82</td>
<td>60.3</td>
<td>33.8</td>
<td>1173-1173 a</td>
<td></td>
</tr>
<tr>
<td>Y $\perp^a$</td>
<td>hcp</td>
<td>5.2</td>
<td>67.1</td>
<td>37.6</td>
<td>1173-1573 a</td>
<td></td>
</tr>
<tr>
<td>La</td>
<td>fcc</td>
<td>1.5</td>
<td>45.1</td>
<td>37.9</td>
<td>937-1110 b</td>
<td></td>
</tr>
<tr>
<td>Ce</td>
<td>fcc</td>
<td>0.6</td>
<td>36.6</td>
<td>34.3</td>
<td>800-970 c</td>
<td></td>
</tr>
<tr>
<td>Er $\parallel$</td>
<td>hcp</td>
<td>3.7</td>
<td>72.05</td>
<td>40.4</td>
<td>1475-1685 d</td>
<td></td>
</tr>
<tr>
<td>Er $\perp$</td>
<td>hcp</td>
<td>4.5</td>
<td>72.27</td>
<td>40.5</td>
<td>1475-1685 d</td>
<td></td>
</tr>
<tr>
<td>Yb</td>
<td>hcp</td>
<td>3.4x10$^{-2}$</td>
<td>35.06</td>
<td>32.1</td>
<td>800-990 e</td>
<td></td>
</tr>
</tbody>
</table>

a. $\parallel$ and $\perp$ represent directions parallel and perpendicular to the c axis.

a. Gornyy and Al'tovskiy (1970)
b. Dariel et al. (1969b)
c. Dariel et al. (1971)
d. Spedding and Shiba (1972)
e. Fromont et al. (1974)
<table>
<thead>
<tr>
<th>Element</th>
<th>$D_0$</th>
<th>$Q$</th>
<th>$Q/T_m$</th>
<th>Temperature Interval (K)</th>
<th>$\Delta V$</th>
<th>$\Delta V/V_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>La</td>
<td>1.3x10^{-2}</td>
<td>24.5</td>
<td>20.5</td>
<td>1140-1173 (a)</td>
<td>1143-1183 (b)</td>
<td>2.20 (c)</td>
</tr>
<tr>
<td>Ce</td>
<td>1.2x10^{-2}</td>
<td>21.5</td>
<td>20.0</td>
<td>1000-1073 (d)</td>
<td>1000-1073 (e)</td>
<td>-2.1 (f)</td>
</tr>
<tr>
<td>Pr</td>
<td>8.7x10^{-2}</td>
<td>29.4</td>
<td>24.3</td>
<td>1050-1200 (g)</td>
<td>0 (c)</td>
<td>~0</td>
</tr>
<tr>
<td>Gd</td>
<td>8.5x10^{-3}</td>
<td>32.2</td>
<td>20.3</td>
<td>1538-1585 (h)</td>
<td>773-1073 (h)</td>
<td></td>
</tr>
<tr>
<td>Eu</td>
<td>1</td>
<td>34.5</td>
<td>31.4</td>
<td>773-1073 (h)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Yb</td>
<td>0.12</td>
<td>28.9</td>
<td>26.3</td>
<td>1003-1073 (i)</td>
<td>15.7 (j)</td>
<td>0.59</td>
</tr>
<tr>
<td>Pu*</td>
<td>3x10^{-3}</td>
<td>15.7</td>
<td>17.2</td>
<td>773-885 (k)</td>
<td>-4.9 (l)</td>
<td>-0.34</td>
</tr>
</tbody>
</table>

*Non rare-earth metal.

a. Dariel (1973)  
g. Dariel et al. (1969a)  
b. Languille et al. (1974b)  
h. Fromont (1975a)  
c. Boidron (1975)  
i. Fromont et al. (1974)  
d. Dariel et al. (1971)  
j. Fromont (1975b)  
e. Languille et al (1973)  
k. Dupuy and Calais (1968)  
f. Languille et al (1974a)  
l. Cornet (1971)
Table 12.3

Metallic Solute Diffusion in Rare-Earth Metals

<table>
<thead>
<tr>
<th>Solvent Matrix</th>
<th>Solute</th>
<th>$D_0$ ( \text{cm}^2/\text{sec} )</th>
<th>$Q$ ( \text{kcal/mol} )</th>
<th>$K = \frac{D_{\text{Solute}^+}}{D_{\text{Self}}} )</th>
<th>Diffusivity*</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y-α, hcp</td>
<td>Zr</td>
<td>4 ( \times 10^{-3} )</td>
<td>38</td>
<td>12</td>
<td>?</td>
<td>a</td>
</tr>
<tr>
<td></td>
<td>59 Fe</td>
<td>1.8 ( \times 10^{-2} )</td>
<td>20</td>
<td>( 2 \times 10^4 )</td>
<td>F</td>
<td>b</td>
</tr>
<tr>
<td></td>
<td>110 Ag</td>
<td>5.4 ( \times 10^{-3} )</td>
<td>18</td>
<td>( 10^4 )</td>
<td>F</td>
<td>b</td>
</tr>
<tr>
<td>La-β, fcc</td>
<td>198 Au</td>
<td>2.2 ( \times 10^{-2} )</td>
<td>18.1</td>
<td>( 3.5 \times 10^3 )</td>
<td>F</td>
<td>c</td>
</tr>
<tr>
<td>La-γ, bcc</td>
<td>141 Ce</td>
<td>1.8 ( \times 10^{-2} )</td>
<td>25</td>
<td>1.2</td>
<td>N</td>
<td>d</td>
</tr>
<tr>
<td>Ce-γ, fcc</td>
<td>110 Ag</td>
<td>2.5 ( \times 10^{-2} )</td>
<td>21.1</td>
<td>( 1.2 \times 10^2 )</td>
<td>F</td>
<td>e</td>
</tr>
<tr>
<td></td>
<td>198 Au</td>
<td>4.4 ( \times 10^{-3} )</td>
<td>14.9</td>
<td>( 5 \times 10^2 )</td>
<td>F</td>
<td>e</td>
</tr>
<tr>
<td></td>
<td>110 Ag</td>
<td>1.4</td>
<td>28</td>
<td>( 2 \times 10^2 )</td>
<td>F</td>
<td>f</td>
</tr>
<tr>
<td></td>
<td>60 Co</td>
<td>1 ( \times 10^{-2} )</td>
<td>11</td>
<td>( 2.7 \times 10^4 )</td>
<td>F</td>
<td>f</td>
</tr>
<tr>
<td></td>
<td>59 Fe</td>
<td>3.3 ( \times 10^{-4} )</td>
<td>46</td>
<td>( 2.6 \times 10^4 )</td>
<td>F</td>
<td>f</td>
</tr>
<tr>
<td></td>
<td>59 Fe</td>
<td>1.7 ( \times 10^{-2} )</td>
<td>11.9</td>
<td>( 10^4 )</td>
<td>F</td>
<td>g</td>
</tr>
<tr>
<td>Solvent Matrix</td>
<td>Solute</td>
<td>$D_0$ cm$^2$/sec</td>
<td>$Q$ kcal/mol</td>
<td>$K = \frac{D_{\text{Solute}^+}}{D_{\text{Self}}}$</td>
<td>Diffusivity*</td>
<td>Ref.</td>
</tr>
<tr>
<td>----------------</td>
<td>---------</td>
<td>------------------</td>
<td>--------------</td>
<td>---------------------------------</td>
<td>--------------</td>
<td>------</td>
</tr>
<tr>
<td>Ce–δ, bcc</td>
<td>$^{110}$Ag</td>
<td>$1.2 \times 10^{-1}$</td>
<td>22.2</td>
<td>16</td>
<td>F</td>
<td>e</td>
</tr>
<tr>
<td></td>
<td>$^{198}$Au</td>
<td>$9.5 \times 10^{-2}$</td>
<td>20.5</td>
<td>10</td>
<td>F</td>
<td>e</td>
</tr>
<tr>
<td></td>
<td>$^{59}$Fe</td>
<td>$2 \times 10^{-3}$</td>
<td>7.7</td>
<td>17</td>
<td>F</td>
<td>g</td>
</tr>
<tr>
<td></td>
<td>$^{140}$La</td>
<td>$1.3 \times 10^{-2}$</td>
<td>24.5</td>
<td>0.75</td>
<td>N</td>
<td>h</td>
</tr>
<tr>
<td>Pr–α, dhcp</td>
<td>$^{64}$Cu</td>
<td>$8.4 \times 10^{-2}$</td>
<td>18.1</td>
<td>$8 \times 10^3$</td>
<td>F</td>
<td>i</td>
</tr>
<tr>
<td></td>
<td>$^{110}$Ag</td>
<td>$1.4 \times 10^{-1}$</td>
<td>25.4</td>
<td>$3.5 \times 10^2$</td>
<td>F</td>
<td>j</td>
</tr>
<tr>
<td></td>
<td>$^{198}$Au</td>
<td>$4.3 \times 10^{-2}$</td>
<td>19.7</td>
<td>$1.8 \times 10^3$</td>
<td>F</td>
<td>j</td>
</tr>
<tr>
<td></td>
<td>$^{60}$Co</td>
<td>$4.7 \times 10^{-2}$</td>
<td>16.4</td>
<td>$10^4$</td>
<td>F</td>
<td>j</td>
</tr>
<tr>
<td></td>
<td>$^{59}$Fe</td>
<td>$2.1 \times 10^{-3}$</td>
<td>9.4</td>
<td>$1.1 \times 10^4$</td>
<td>F</td>
<td>g</td>
</tr>
<tr>
<td></td>
<td>$^{65}$Zn</td>
<td>$1.8 \times 10^{-1}$</td>
<td>24.8</td>
<td>$5 \times 10^2$</td>
<td>F</td>
<td>k</td>
</tr>
<tr>
<td>Pr–β, bcc</td>
<td>$^{64}$Cu</td>
<td>$5.7 \times 10^{-2}$</td>
<td>17.8</td>
<td>$10^2$</td>
<td>F</td>
<td>i</td>
</tr>
<tr>
<td></td>
<td>$^{110}$Ag</td>
<td>$3.2 \times 10^{-2}$</td>
<td>21.5</td>
<td>8</td>
<td>F</td>
<td>j</td>
</tr>
<tr>
<td></td>
<td>$^{198}$Au</td>
<td>$3.3 \times 10^{-2}$</td>
<td>20.1</td>
<td>16</td>
<td>F</td>
<td>j</td>
</tr>
<tr>
<td></td>
<td>$^{65}$Zn</td>
<td>$6.3 \times 10^{-1}$</td>
<td>27.0</td>
<td>15</td>
<td>F</td>
<td>k</td>
</tr>
</tbody>
</table>
Table 12.3 (cont.)

<table>
<thead>
<tr>
<th>Solvent Matrix</th>
<th>Solute</th>
<th>$D_0$ cm$^2$/sec</th>
<th>$Q$ kcal/mol</th>
<th>$K = \frac{D_{\text{Solute}}}{D_{\text{Self}}}$</th>
<th>Diffusivity*</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pr-$\beta$, bcc</td>
<td>$^{59}$Fe</td>
<td>$4 \times 10^{-3}$</td>
<td>10.4</td>
<td>$10^2$</td>
<td>F</td>
<td>g</td>
</tr>
<tr>
<td></td>
<td>$^{140}$La</td>
<td>$1.8 \times 10^{-2}$</td>
<td>25.7</td>
<td>1</td>
<td>N</td>
<td>l</td>
</tr>
<tr>
<td></td>
<td>$^{166}$Ho</td>
<td>$9.5 \times 10^{-3}$</td>
<td>26.3</td>
<td>0.3</td>
<td>N</td>
<td>l</td>
</tr>
<tr>
<td></td>
<td>$^{114}$In</td>
<td>$9.6 \times 10^{-2}$</td>
<td>28.9</td>
<td>1.1</td>
<td>N</td>
<td>l</td>
</tr>
<tr>
<td>Nd-$\alpha$, dhcp</td>
<td>$^{59}$Fe</td>
<td>$4.6 \times 10^{-3}$</td>
<td>12.2</td>
<td></td>
<td>F</td>
<td>g</td>
</tr>
<tr>
<td>Nd-$\beta$, bcc</td>
<td>$^{59}$Fe</td>
<td>$1.0 \times 10^{-2}$</td>
<td>13.6</td>
<td></td>
<td>F</td>
<td>g</td>
</tr>
</tbody>
</table>

Footnotes to Table 12.3.

*Ratio of solute diffusivity to self-diffusion in the solvent matrix at the highest measured temperature.

* N stands for normal diffusion, presumably the same mechanism for solute and self-diffusion; F stands for fast-diffusion with a partly interstitial component for solute diffusion.

a. Rogozin et al. (1968)  e. Dariel et al. (1972)  i. Dariel (1971)
b. Murphy et al. (1975)  f. Cathey et al. (1973)  j. Dariel, et al. (1969c)
d. Fromont (1975)  h. Dariel (1973)  l. Dariel et al. (1969a)
Table 12.4. Compilation of the Direction of Electrotransport of Various Solutes in Rare-Earth Metals.

<table>
<thead>
<tr>
<th>Solvent Rare-Earth</th>
<th>Solute</th>
<th>Sign of*</th>
<th>Ref.</th>
<th>Solvent Rare-Earth</th>
<th>Solute</th>
<th>Sign of*</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>La</td>
<td>Fe</td>
<td>-</td>
<td>a</td>
<td>Gd</td>
<td>0</td>
<td>-</td>
<td>e</td>
</tr>
<tr>
<td></td>
<td>Al,Cu,Mn</td>
<td>+</td>
<td>a</td>
<td></td>
<td>0</td>
<td>-</td>
<td>f</td>
</tr>
<tr>
<td>Ce</td>
<td>Mn,Fe,Co,Ni,Cu</td>
<td>-</td>
<td>b</td>
<td>Si</td>
<td>+</td>
<td>f</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Mo</td>
<td>+</td>
<td>b</td>
<td>C,N,O</td>
<td>-**</td>
<td>g</td>
<td></td>
</tr>
<tr>
<td></td>
<td>O,Mn,Fe</td>
<td>-</td>
<td>a</td>
<td>Tb</td>
<td>N,O</td>
<td>-</td>
<td>h</td>
</tr>
<tr>
<td></td>
<td>Cu,Mo</td>
<td>+</td>
<td>a</td>
<td>Lu</td>
<td>C,N,O</td>
<td>-**</td>
<td>i</td>
</tr>
<tr>
<td></td>
<td>Fe,Co</td>
<td>-**</td>
<td>c</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ag</td>
<td>+**</td>
<td>c</td>
<td>Y</td>
<td>N,O</td>
<td>-</td>
<td>j</td>
</tr>
<tr>
<td>Pr</td>
<td>Fe</td>
<td>-</td>
<td>a</td>
<td>Mn,Fe,Co,Ni</td>
<td>-</td>
<td>j</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Cu</td>
<td>+</td>
<td>a</td>
<td>H,C,N,O</td>
<td>-**</td>
<td>k</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ag</td>
<td>-</td>
<td>d</td>
<td>Fe</td>
<td>-**</td>
<td>l</td>
<td></td>
</tr>
</tbody>
</table>

* (-) stands for anode directed and (+) for cathode directed solutes.

** Quantitative results.

a. Marchant et al. (1971)  
g. Peterson and Schmidt (1972)
b. Moore et al. (1965)  
h. Jordan et al. (1975)
c. Cathey et al. (1973)  
i. Peterson and Schmidt (1969)
d. Tessler and Dariel (1973)  
j. Williams and Huffine (1961)
e. Graham (1967)  
k. Carlson et al. (1966)
f. Jordan and Jones (1973)  
l. Murphy et al. (1975)
Table 12.5

Mobilities, Diffusion Coefficients and Purification Factor of Metalloid Solutes at 0.9 $T_m$

<table>
<thead>
<tr>
<th>Solutes</th>
<th>U($10^{-5}$ cm$^2$/sec.V)</th>
<th>D($10^{-5}$ cm$^2$/sec)</th>
<th>U/D (V$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\alpha$-Gd</td>
<td>Lu</td>
<td>$\alpha$-Y</td>
</tr>
<tr>
<td>C</td>
<td>3.4</td>
<td>4.2</td>
<td>15.0</td>
</tr>
<tr>
<td>N</td>
<td>5.1</td>
<td>14.0</td>
<td>14.0</td>
</tr>
<tr>
<td>O</td>
<td>19.0</td>
<td>39.0</td>
<td>39.0</td>
</tr>
</tbody>
</table>

+ The results for Gd, Lu any Y have been compiled by Carlson et al. (1975).

* Results of internal friction studies in the 20 - 300°C temperature range extrapolated to 0.9 $T_m$ of Ce (Borisov et al. 1971).
Table 12.6
Diffusion Studies of Rare-Earth Solutes in Various Metals

<table>
<thead>
<tr>
<th>Solvent Metal</th>
<th>Solute</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag, Pb</td>
<td>Ce, Nd, Pm</td>
<td>Williams and Slifkin (1963)</td>
</tr>
<tr>
<td>Al</td>
<td>La, Ce, Pr, Nd, Sm</td>
<td>Murarka and Agarwala (1968)</td>
</tr>
<tr>
<td>Zr</td>
<td>Ce</td>
<td>Paul et al. (1968)</td>
</tr>
<tr>
<td>Cu</td>
<td>Ce, Pm, Eu, Tb, Tm, Lu</td>
<td>Badrinarayanan and Mathur (1970)</td>
</tr>
<tr>
<td>Ni</td>
<td>Ce, Nd</td>
<td>Paul and Agarwala (1971)</td>
</tr>
<tr>
<td>Mo, W, Nb, Ta</td>
<td>Y</td>
<td>Gornyy and Al'tovskiy (1971)</td>
</tr>
</tbody>
</table>
FIGURE CAPTIONS

Fig. 1. Self-diffusion coefficients of La, Ce, Pr and Yb as function of the inverse temperature.

Fig. 2. The activation energy for self-diffusion as function of the melting temperature of bcc and fcc metals.

Fig. 3. Self-diffusion of bcc metals as function of relative temperature.

Fig. 4. The diffusivities of various solutes in fcc and bcc Ce as function of the inverse temperature.

Fig. 5. The diffusivities of various solutes in double-hcp and bcc Pr as function of the inverse temperature.
Fig. 12.1
Fig. 12.2
Fig. 12.3
Fig. 12.4
Fig. 12.5
activated interstitial model 12.3.3
amorphous alloy formation 12.4
activation energies (see diffusion)
anisotropic diffusion 12.3.1
cerium
electrotransport in 12.5
self-diffusion in 12.3
solute diffusion in 12.4
diffusion 12
activation energies for self- 12.3
activation energies for solute- 12.4
anomalous, in bcc metals 12.3.2
anisotropic 12.3.1
chemical 12.6.1
compounds 12.6.3
experimental techniques 12.2
fast 12.4
rare-earth solutes in metals 12.6.2
self- 12.3
solute in rare-earth metals 12.4
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effective charge 12.5
electromigration 12.5
electrotransport 12.5
Engel-Brewer correlation theory 12.3.4
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self-diffusion in 12.3.1
europium
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gadolinium
electrotransport in 12.5
self-diffusion in 12.3.2
internal friction 12.5
interstitial mechanism 12.4
Kirkendall effect 12.6.1
lanthanum
enthalpy of vacancy formation 12.3.1
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solute diffusion in 12.4
lutetium
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solute diffusion in 12.4
plutonium
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praseodymium
self-diffusion in 12.3
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sintering 12.6.3
SmCo$_5$- sintering mechanism 12.6.3
terbium
electrotransport in 12.5
ytterbium
self-diffusion in 12.3
yttrium
electrotransport in 12.5
solute diffusion in 12.3
solute diffusion in 12.5
vacancy mechanism 12.3, 12.4
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