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LOCAL MOMENT ON Ru ATOMS IN Ni AND GIANT INDUCED KSHTFTS ABOVE THE CURIE POINT

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LOCAL MOMENT ON Ru ATOMS IN Ni AND GIANT INDUCED KNIGHT SHIFTS ABOVE THE CURIE POINT

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This letter has four purposes: (1) to extend the model recently proposed by Jaccarino, Walker, and Wertheim\(^1\) (JWW) for hyperfine fields arising in part from local moments on solutes in ferromagnetic lattices to include effects of (nonlocal) polarized conduction electrons; (2) to report the first case so detected of a local moment for a 4d atom (Ru) in a 3d host (Ni), and a case (Cd in Ni) for which a local moment is not strongly indicated; (3) to demonstrate the existence of enhanced Knight shifts of the order of 90\% for solute Ru and Cd atoms in Ni above the Curie point; (4) to report evidence for a decrease in local magnetization relative to lattice magnetization above the Curie point.

Time-differential and integral perturbed angular correlation in Ru\(^{99}\) and Cd\(^{111}\) was the experimental technique used throughout. Both demagnetized\(^2\) and polarized samples were used below the Curie point. Above \(T_C\), polarizing fields of 19.5 kG were applied to the sample. This is the first instance in which differential angular correlations have been used in a study of local moments, and we wish to emphasize that the applicability of this technique is independent of temperature and applied magnetic field.

In the JWW model the temperature dependence of the NMR frequency for a solute atom in a ferromagnetic lattice is explained by associating the hyperfine field with a local moment. This moment is coupled to the lattice magnetization less strongly than are those of the host atoms. The coupling strength is given by the parameter \(\xi\) times the molecular field of the host. The hyperfine field
of the solute is thus proportional to the Brillouin function \( B_J(y) \), with
\[
y = \zeta \frac{\sigma_T}{\sigma_0} \frac{T_c}{T}.
\]
The JWW model then employs two parameters, \( J \) and \( \zeta \). With this model these authors \(^1\) were able to obtain an excellent fit of the NMR data of Koi et al.\(^3\) on Mn in Fe, using \( \zeta = .731 \) and \( J = 3/2 \), and less satisfactory fits for other spins. Because contributions of non-local electrons were not considered, we cannot regard this fit as evidence for a spin of \( 3/2 \) on Mn in Fe.

The model can be extended to account for the important effect of polarized non-local (conduction) electrons on the hyperfine field by considering a third parameter, \( (1-f) = \frac{H_N(O)}{H_{hf}(O)} \), which describes the fraction of \( H_{hf}(O) \), the hyperfine field on the impurity at absolute zero, that arises from nonlocalized electrons. We assume that the non-local part of the hyperfine field varies directly with lattice magnetization and write

\[
H_{hf}(T) = H_N(O) \frac{\sigma_T}{\sigma_0} + H_L(O) B_J(y)
\]

or

\[
\frac{H_{hf}(T)}{H_{hf}(0)} = (1-f) \frac{\sigma_T}{\sigma_0} + f B_J(y)
\]

There is an unambiguous way to determine the parameters \( y \) and \( f \) from the experimental data \( H_{hf}(T)/H_{hf}(0) \). If we define the reduced quantities

\[
\frac{H_{hf}(T)}{H_{hf}(0)}/\frac{\sigma_T}{\sigma_0} = H^R \quad \text{and} \quad \frac{B_J(y)}{\frac{\sigma_T}{\sigma_0}} = B^R_J(y)
\]

then Eq. (2) can be rewritten in the form

\[
B^R_J(y) = \frac{1}{f} H^R + \frac{(f-1)}{f}.
\]

\[\text{(4)}\]
The only acceptable value of $\xi$ is the one for which $E_J^R(y)$ vs $H_R$ is a straight line. The parameter $f$ is then obtained from the slope and the zero intersection of this line. According to its definition, the value of $f$ may be less (or greater) than one, indicating that the local and the non-local parts of the hyperfine field are parallel (or antiparallel).

We have varied $\xi$ and $f$ for the Mn in Fe case treated by Jaccarino et al. and have found very good fits for $H_{hf}(T)$ for several values of $J$. For $J = 5/2$, e.g., the best values for $\xi$ and $f$ are 0.95 and 1.104, respectively. This means that in this case the local moment field is antiparallel to the non-local field of the polarized electrons. Although the model does not favor any particular value of $J$, it does stress for Mn in Fe the possible importance of a non-local electron contribution of the order of 10%. However, the major conclusion reached by Jaccarino et al., namely that a local moment is present, remains unchanged.

If a local moment in a 3d-element magnetic lattice is found for solute manganese, which itself is a 3d element and exhibits antiferromagnetism, it is very interesting to determine whether the hyperfine field of a solute 4d element such as Ru, which does not exhibit collective magnetism in its own lattice, will show "local moment" behavior or will vary with temperature simply as the lattice magnetization. It has been suggested from a study of the systematics of hyperfine fields in an iron lattice that the Ru in Fe field arises in large part from core polarization. A similar statement can be made for Ru in Ni. On the other hand the approximate proportionality between solute hyperfine field and host magnetization for most non-3d solutes in Fe and Ni, which is certainly not present for Mn, underscores the fact that this field is induced by the host lattice and raises doubts that the field can be weakly coupled to the lattice magnetization.
In Fig. 1 are shown the variations with $T/T_C$ of the hyperfine fields of Ru and Cd in a Ni host in concentrations less than 1%. For Ru, $H_{hf}(T)$ falls well below the magnetization curve of pure Ni, while for Cd it is much closer. Curves A and B fit the Ru data equally well with the parameter sets $\zeta = 0.86$, $f = 0.543$, $J = 5/2$, and $\zeta = 0.40$, $f = 0.576$, $J = 1/2$, respectively. The substantial local moment of Ru in Ni probably arises from its open 4d shell. The fact that $f < 1$ indicates that the local part of the hyperfine field is parallel to the non-local part. Similar behavior may be expected for other 4d and 5d atoms in ferromagnetic lattices, especially in view of the systematic variation of the magnitudes of these fields in excess of the magnitudes expected from conduction electron polarization alone, their usually negative signs, and their tendency to peak in the middle of the d shells.\textsuperscript{4,5,6} It will be interesting to see whether the angular correlation and NMR frequencies of these elements as solutes follow the behavior implied by Eq. (1). For Cd with a filled 4d shell the hyperfine field is apparently of non-local origin. The hyperfine field follows the magnetization curve of Ni rather closely, and the local moment model is not applicable. It is in fact impossible to find an unambiguous set of parameters $\zeta$, $f$, and $J$.

No simple independent test of the predictions of this model seems to be available below the Curie point, as can readily be ascertained by examining the structure of Eq. (1). In the ferromagnetic state $\sigma_T$ depends on $T$ alone; thus for a particular set of values of $\zeta$, $f$, and $J$ each term in Eq. (1) is completely specified by $T$. Above $T_C$ this restriction is removed and we may vary $\sigma_T$, $H_{ext}$ and $T$ independently over a wide range by controlling the applied magnetic field and employing the known dependence of magnetization of a nickel lattice on applied field and temperature.\textsuperscript{7} The effective field experienced by the solute nucleus is then given (after correction for contributions from Lorentz and demagnetizing fields) by
To calculate $H_{hf}$ for any $H_{ext}$ and $T$ we first assume that Eq. (1) is still valid in the paramagnetic region if we replace the spontaneous magnetization of the lattice, $\sigma_T$, by the induced magnetization $\sigma_T, H_{ext}$. Using the values of $\zeta$, $f$, and $J$ determined from the fit below the Curie point, the hyperfine field $H_{hf}(\sigma_T, H_{ext}, T)$ above the Curie point can be calculated and compared with the experimental data. This will provide a very sensitive test of the validity of the extended JWJ model above the Curie point.

Experimentally, one expects to observe a shift $(H_{eff} - H_{ext})/H_{ext} = \beta - 1$ which is analogous to Knight shifts in NMR. There are, however, several differences between this effect and the usual Knight shift that should be emphasized: (1) the host lattice is magnetized by $H_{ext}$ and collective magnetic interactions near the Curie point greatly enhance this magnetization; (2) there are two mechanisms, local and non-local (Eq. (1)), for polarization of electrons at the solute; and (3) the polarized electrons produce a hyperfine field at the solute nucleus primarily via direct and induced contact interaction (core polarization). The quality factors of the resonances in Ru and Cd are not sufficient to permit a detailed study, but we have used these nuclei to confirm the major features of the effect discussed above, which is expected to be of the order of 100% rather than the more usual 0-5% Knight shifts seen in NMR. Further, the shift should be negative, as predicted from the negative $H_{hf}$ observed below the Curie point.

The results are shown in Fig. 2. For both Ru and Cd we have plotted the two possible extremes for the hyperfine field: $H_{hf} = 0$ (curve A); and $H_{hf} = \left[ (\sigma_T, H_{ext}) / (\sigma_0) \right] H_{hf}(0)$ i.e., completely non-local (curve B).
local and non-local part of the field is the same as below $T_C$, the data must lie between the curves A and B. With the parameter set $\zeta$, $f$, and $J$ which fit the data below the Curie point, curve C is obtained using Eqs. (2) and (5). This curve should fit the data if Eq. (2) could be applied, with no modification, above $T_C$. It falls substantially below the data, predicting shifts that are too large. If we assume that the local part of the field vanishes above the Curie point ($B_J(y) = 0$) while the non-local contribution remains unchanged we obtain from Eq. (2), $H_{hf} = 0.457 \left[ (\sigma_{T,H_{ext}})/(\sigma_0) \right] H_{hf}(0)$ (curve D). These comments apply independent of $J$ as the model is very insensitive to the spin of the local moment.

A comparison of the Cd data above the Curie point with the prediction of Eq. (2) could not be done because the model does not apply to Cd in Ni. The measured shifts are, however, much closer to the predicted curve (B) based on a completely non-local $H_{hf}$ than is the case for Ru in Ni. This behavior is consistent with the fact that Cd follows the magnetization curve more closely below $T_C$. We regard this as an important qualitative confirmation of the model.

The relation between the magnetization of the local moment on a solute and the host magnetization probably differs above and below $T_C$. Short relaxation times and the absence of stationary domains should combine to lessen the influence of the local moment relative to host magnetization in the paramagnetic region. The shifts discussed above bear out this expectation. Since even curve D, which represents only non-local contributions to $H_{hf}$, predicts shifts larger than experimentally observed, it is evident that the non-local part of the hyperfine field is also attenuated.

We may from these data predict with some confidence that the recently observed NMR of Ru, Rh, and Pd in Fe should show local moment temperature dependencies, that the fields are negative, and that negative Knight shifts of several tens percent should be observable above $T_C$. 
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REFERENCES


6. Recent NMR measurements by M. Kontani, K. Asayama, and J. Itoh (private communication, August 1965) on Y, Mo, Rh, and Pd in an iron lattice indicate, together with the results presented in Refs. 4 and 5, a definite tendency for the magnitudes of $H_{hf}$ at the impurity to go through a maximum near Pd.


9. O. C. Kistner, (private communication) indicates that the internal field of Ru in Fe is negative.
Fig. 1. Temperature variation of $H_{hf}$ for Ru and Cd in Ni, determined by time-differential angular correlations of gamma-ray cascades in Ru$^{99}$ and Cd$^{111}$. Two theoretical curves for Ru, based on the extended JWW model are shown; curve A using $\zeta = 0.86, f = 0.543, J = 5/2$ and curve B using $\zeta = 0.40, f = 0.576, J = 1/2$. Both fit the data within the limits of error indicating that the extended JWW model is insensitive to J. The large decoupling of the $H_{hf}(T)$ curve from the magnetization curve of Ni establishes the existence of a local moment unambiguously. The Cd data are too close to the magnetization curve to warrant interpretation on this model.

Fig. 2. Giant induced Knight shifts for Ru and Cd in Ni above the Curie point. The temperature dependence of $\beta = H_{eff}/H_{ext}$ was measured with a polarizing field of 19.5 kG. Curves A to D represent different theoretical expectations for the hyperfine field: $H_{hf} = 0$ (curve A); $H_{hf} = \left[\sigma_{T,H_{ext}}/\sigma_0\right]H_{hf}(0)$ (curve B); $H_{hf} = H_{hf}(0) [\left(1-f\right)\sigma_{T,H_{ext}}/\sigma_0 + f B(y)]$ with $\zeta = 0.86, f = 0.543, and J = 5/2$ (curve C); $H_{hf} = H_{hf}(0) \left(1-f\right)\sigma_{T,H_{ext}}/\sigma_0$ with $f = 0.543$ as for C (curve D).
Fig. 1

\[ \frac{H_{hf}(T)}{H_{hf}(4.2)} \]

\[ T/T_C \]

\[ \sigma_T/\sigma_0 (\text{Ni}) \]

\[ \phi^{99}\text{Ru} \]

\[ \phi^{111}\text{Cd} \]
Fig. 2
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