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OBSERVATION OF ZERO-POINT ATOMIC MOTION NEAR THE Cr (110) SURFACE
BY LOW-TEMPERATURE DIFFRACTION OF SLOW ELECTRONS

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ABSTRACT

Low energy electron diffraction studies of the (110) chromium surface at temperatures as low as one-sixth the Debye temperature are described. Measurement of the temperature and energy dependence of the diffracted intensity was found to be improved by modulation of the incident energy and phase sensitive detection. Zero-point thermal motion of atoms near the surface, and the temperature dependence of the ratio of surface to bulk mean square displacements, have been observed.

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The present work is concerned with the temperature and energy dependence of the diffracted intensity in low energy electron diffraction (LEED) studies of the (110) face of chromium. The principle new aspects of this work are, first, the measurement of the mean square displacements normal to the surface, for atoms near the surface and in the bulk, at temperatures as low as one-sixth the Debye temperature $\Theta_D$, and second, the application of modulation techniques to the measurement of the diffracted intensity. Intensity data for a large number of diffraction beams were found to be amenable to a single scattering analysis. The experiments have revealed the zero-point contribution to the mean square displacements of atoms near the surface, and the strong temperature dependence of the ratio of surface to bulk mean square displacements at low temperatures. These effects have been predicted theoretically, but not previously observed experimentally.

The chromium specimen was cut parallel to the (110) face of a high-purity single crystal. After mechanical polishing and electropolishing, the specimen was spot-welded to polycrystalline chromium support bars of comparable purity, and mounted in thermal contact with the liquid nitrogen reservoir of a low-temperature sample manipulator. Alterations in the original manipulator design made rapid sequential heating and cooling of the specimen possible. Temperature was monitored by a chromel-alumel thermocouple welded to the back of the specimen. The LEED apparatus was of the conventional post-acceleration type; thus diffraction beam intensity measurements were made using a telephotometer aimed at the fluorescent screen. Both transient and steady-state methods were used to obtain the temperature dependence of the diffracted intensity. Measurements were made in the temperature range $100-900\,^\circ\text{K}$. 
Clean, unfaceted (110) surfaces were obtained primarily by heating the specimen in the neighborhood of 1000°C, although bombardment by 450 V argon or xenon ions, which was also employed, may have aided the cleaning process. The resulting surfaces yielded sharp, low-background diffraction patterns which indexed to an atomic array of symmetry and dimensions identical, within experimental error, to an internal (110) plane of atoms. The energy dependence of the intensity was recorded for the (0 0), (1 0), (1 1), (0 2), (1 2), and (2 2) diffraction beams. For the (0 0) beam the angle of incidence was 86°; for all of the other beams it was 90°. In Fig. 1, the values of the accelerating potential V' at which intensity maxima were observed are plotted vs F(n 1, n 2, n 3), a function of the beam indices n 1, n 2, and the index n 3 identifying the Bragg peaks. This method for analyzing intensity data is described elsewhere. It determines for chromium an inner potential V 0 = -16 volts, and a lattice parameter within 1% of the bulk value. Above about 50 eV incident energy, subsidiary peaks in the intensity data (not plotted in Fig. 1), were at least an order of magnitude weaker than the Bragg peaks. Below V'~ 50 eV, the strength of the subsidiary intensity structure varied strongly with the angle of incidence, and was therefore easily identifiable. These results, taken together, provide evidence for the preponderance of single scattering at values of V' corresponding to the Bragg peaks.

A portion of a typical intensity spectrum for the (0 0) diffraction beam is shown at the top of Fig. 2. In analyzing the temperature dependence of the diffracted intensity, it is necessary to eliminate the contribution of the background. Accurate determination of the latter can be difficult, and is a source of uncertainty in the analysis. If a small amplitude modulation is impressed on the energy of the incident electrons, the signal observed using
a lock-in amplifier tuned to the modulation frequency is proportional to $dI/dV'$, the derivative of intensity with respect to the accelerating potential. Assuming the widths and shapes of the intensity peaks are not temperature dependent, as is normally the case in LEED, the peak intensity is proportional to the difference between maximum and minimum values of $dI/dV'$. This measurement automatically excludes background contributions that are constant, or that vary linearly with $V'$ over the voltage range needed to span the intensity peak.

Of several modulation methods tried, the one found most satisfactory employs capacitive coupling of a sinusoidal audio signal directly to the cathode of the LEED electron gun and to the suppressor grid of the LEED optics. In this approach, the energy analysis of the back-scattered electrons is not disturbed by the modulation. The signal is obtained by tapping into the photomultiplier circuit of the telephotometer and coupling directly to a lock-in amplifier. The output is presented to an X-Y recorder in the usual manner. A modulation amplitude of about one-tenth the intensity peak width, and frequency in the neighborhood of 111 Hz, have been used. In Fig. 2, corresponding portions of intensity and $dI/dV'$ spectra for the (0 0) diffraction beam are shown.

Employing both normal and modulation techniques, the temperature dependence of the (0 0) beam intensity has been investigated for an angle of incidence of 86°. Neglecting the slight departure from normal incidence, the temperature dependence is given by

$$I = A \exp \left[ - \frac{16\pi^2}{\lambda^2} \langle u_z^2 \rangle_{\text{eff}} \right]$$

where $A$ is a constant, and $\langle u_z^2 \rangle_{\text{eff}}$ is the mean square atomic displacement.
normal to the surface, averaged over the region of the crystal penetrated by the incident electrons. The wavelength $\lambda$ of the electrons inside the specimen is given in Angstrom units by

$$\lambda = \left(\frac{150.4}{V}\right)^{\frac{1}{2}} = \left(\frac{150.4}{(V' - V_0)}\right)^{\frac{1}{2}}$$

with $V$ the energy, in eV, of the incident electrons inside the crystal. For each Bragg peak, the data have been plotted as $\ln I$ vs $T$, the sample temperature. The constants $\ln A$ have been evaluated using the theoretical prediction that, at high temperature, $\ln I$ is proportional to $-T$ and extrapolates linearly to zero at $0^\circ$K. In this manner, $\langle u_z^2 \rangle_{\text{eff}}$ has been obtained as a function of $T$, for six values of $V$ corresponding to the second through the seventh Bragg peaks. At successively higher values of $V$, the slope of the linear region at high temperatures was observed to decrease, while curvature appeared at low temperatures. The results for the lowest and highest values of $V$ are shown in Fig. 3.

Calculations for fcc crystals indicate that the linear dependence of $\langle u_z^2 \rangle$ on $T$ persists down to temperatures of the order of one-third $\theta_D$, below which the approach of $\langle u_z^2 \rangle$ toward its zero-point value becomes apparent. Analogous calculations for bcc crystals such as chromium are not yet available, but the results are expected to be qualitatively similar. The data for the six Bragg peaks indicate that at $V = 435$ eV, the incident electrons are penetrating deeply enough to sample essentially bulk values of the atomic displacements, for which $\theta_D \approx 450^\circ$K near room temperature and $\approx 600^\circ$K at 4.2$^\circ$K. However, the electrons with energy $V = 35.5$ eV are scattered near the surface, and the appropriate Debye temperature is considerably smaller. Thus, the observation of curvature below $200^\circ$K in the data for $V = 435$, and the persistence of linearity to at least $150^\circ$K for $V = 35.5$, is consistent with
The quantity \( \frac{\langle u_z^2 \rangle_{\text{surf}}}{\langle u_z^2 \rangle_{\text{bulk}}} \), the ratio of normal components of surface to bulk mean square atomic displacements, has been calculated as a function of temperature for the fcc structure. An experimental estimate of \( \langle u_z^2 \rangle_{\text{surf}} \) may be obtained by extrapolation of the observed dependence of \( \langle u_z^2 \rangle_{\text{eff}} \) on \( V \) to \( V = 0 \). The result is about 6% larger than \( \langle u_z^2 \rangle_{V=35.5} \) determined for the second Bragg peak. Assuming that the result for \( V=435 \) eV is essentially characteristic of the mean square displacement of bulk atoms, the ratio \( \frac{\langle u_z^2 \rangle_{\text{surf}}}{\langle u_z^2 \rangle_{V=435}} \) is plotted vs \( T \) in Fig. 4. The steep rise of this ratio up to temperatures of order one-third the value of \( \Theta_D \) at 0°K, followed by a tapering off toward a constant value, agree with theoretical predictions. This behavior is expected from the plots of Fig. 3, and is a consequence of the increasing importance of low frequency surface modes of vibration as the temperature is increased from 0°K.

Calculations\(^1,2\) for the (100), (110), and (111) surfaces of fcc crystals in the high-temperature limit predict values of \( \frac{\langle u_z^2 \rangle_{\text{surf}}}{\langle u_z^2 \rangle_{\text{bulk}}} \) in the range 2.0-2.4. For bcc crystals, published data\(^9\) are available only for the (100) surface of niobium, for which the value 2.66 is reported. The present work on the (110) surface of chromium yields the value 1.8. It is difficult to assign limits of uncertainty to the latter result since the functional form for the extrapolation of \( \langle u_z^2 \rangle_{\text{eff}} \) to \( V = 0 \) is unknown. However, the value of \( \frac{\langle u_z^2 \rangle_{V=35.5}}{\langle u_z^2 \rangle_{V=435}} = 1.7 \pm 0.12 \) may be taken as a lower limit, since \( \langle u_z^2 \rangle_{V=35.5} \) may still contain substantial contributions from atoms below the surface. It is possible that the use of a Darwin-like model in the analysis\(^10\) of the temperature dependence of the diffracted intensity would be helpful in this matter.
In conclusion, the following points may be noted. First, chromium appears to be a useful material for studies of thermal effects in LEED, due to its high Debye temperature and the relative simplicity of the energy dependence of the diffracted intensity. These properties also make it attractive for surface structure investigations. Second, the method of small-amplitude modulation of the incident electron energy is helpful in studies of diffraction beam intensities, and should be applicable to other LEED problems, particularly when adapted to Faraday collector techniques. And finally, while the observations of the low-temperature behavior of the surface and bulk mean square displacements described above show qualitative agreement with theory, quantitative comparison must await numerical calculations for the bcc structure.

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REFERENCES


Figure Captions

Fig. 1. Values of the accelerating potential for which intensity maxima were observed for the indicated diffraction beams, as a function of $F(n_1, n_2, n_3)$, a quantity related to the phase differences between electrons scattered by the atoms of the crystal. The straight line represents a least-squares fit to the data above $V' = 50$ eV, with the result $V' = -16.1 + 4.44 F(n_1, n_2, n_3)$.

Fig. 2. A portion of the intensity spectrum, and its derivative with respect to energy, for the $(0 0)$ diffraction beam from the $(110)$ surface of chromium. Angle of incidence was $86^\circ$. The fourth, fifth, and sixth Bragg peaks are shown.

Fig. 3. Temperature dependence of the normal component of the effective mean square atomic displacement for the $(110)$ surface of chromium. The electron energy (including inner potential) was 35.5 eV for the upper data, and 435 eV for the lower. The lines are linear fits to the data above 300 K, drawn to include the origin.

Fig. 4. Temperature dependence of the ratio of the normal components of the mean square displacement of surface atoms to the effective mean square displacement determined for $V = 435$ eV.
Figure 1

Graph showing the relationship between accelerating potential $V'$ (Volts) and $F(n_1, n_2, n_3)$. The table lists different beam symbols corresponding to specific beam configurations.
Figure 3

\[ \langle u_2^{\text{eff}} \rangle \times 10^{18} \text{ (cm}^2\text{)} \]

Cr (110)
- \( V = 35.5 \)
- \( V = 435 \)

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Fig. 4

\( \frac{\langle u_z^2 \rangle_{\text{SURFACE}}}{\langle u_z^2 \rangle_{V=435}} \) vs. \( T(\degree K) \)

Cr(110)
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