THERMAL VIBRATIONS OF SURFACE ATOMS

A. U. MacRae and L. H. Germer*
Bell Telephone Laboratories, Murray Hill, New Jersey
(Received May 21, 1962)

We have observed a decrease in the intensity of the low-energy electron diffraction patterns from the surface of clean nickel crystals when the temperature of the crystals is increased. This is the two-dimensional analog of the Debye-Waller effect for solids. Since the diffraction pattern of these low-energy electrons is determined mainly by the topmost layer of surface atoms, observations of this type are capable of revealing information regarding surface vibrational modes. The present results indicate that the vibrational amplitude of surface atoms normal to the surface is greater than the vibrational amplitude of atoms in the bulk of the nickel crystal.

A typical diffraction pattern containing spots upon which intensity vs temperature measurements have been made is reproduced in Fig. 1. This is a back-reflection photograph from the (110) surface of a clean nickel crystal contained in a vacuum system having a background pressure of 3×10^{-10} mm Hg. The pattern was produced by electrons of wavelength 1.07 Å (130 volts) striking the crystal at an angle of 10° with the normal to the surface. Each of these spots exhibit intensity maxima and minima appropriate to the spacings of the atoms in the bulk of the crystal as the wavelength of the incident electrons is changed. This is due to the finite penetration of the incident electron beam into the crystal. It is upon these intensity maxima that the measurements discussed here have been made. Typical results of the temperature variation of the intensity are shown in Fig. 2 for two maxima of the 01 beam. The points in the upper curve are for 294-volt electrons for the intensity maximum having Miller indices 860 and the points in the lower curve are for 150-volt electrons for the 640 maximum. Both plots are normalized to unity at 100°C. In addition to the measurements on these two maxima, the temperature dependence

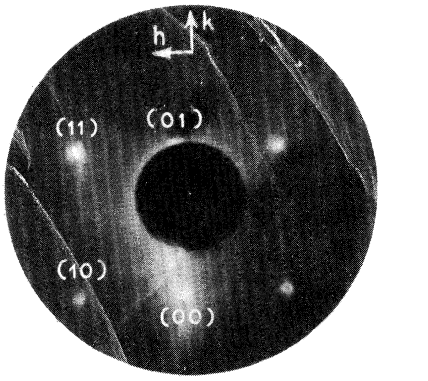

FIG. 1. Diffraction pattern of 130-volt (1.07 Å) electrons from the (110) surface of a clean nickel crystal at room temperature. The measurements in this paper are on the 01 beam, which is slightly obscured by a shield in this picture.

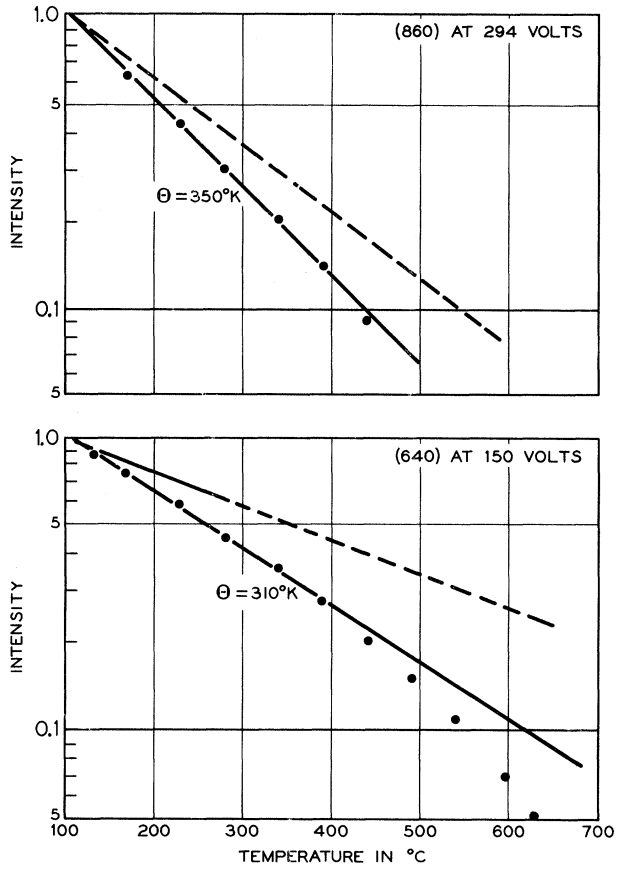

FIG. 2. Temperature variation of the intensity of the 01 beam from a (110) surface of nickel. The dashed curves represent the dependence expected for highly penetrating radiation.

of 18 other maxima from the Ni (110) surface and 12 maxima from a Ni (111) surface have been obtained. These results are consistent with those of Fig. 2.

The dashed curves in the figure represent the variation in the intensity expected for penetrating radiation such as x rays or high-energy electrons and is calculated for the accepted Debye temperature of nickel, 390°K.[1] The Debye temperature obtained with x rays in this manner for metals is usually in close agreement with the Debye temperature obtained by other means.[2] We attribute the deviation of the present measurements from theory to the increased amplitude of vibration of the surface atoms. The slope of these curves can be characterized by a Debye temperature. A low Debye temperature implies a large vibrational amplitude. At high voltages of the incident electrons, measurements of the temperature dependence of the intensity yield a slope in close agreement to that expected for highly penetrating radiation. As the voltage of the incident electrons is decreased, the penetration distance also decreases and surface effects become prominent. Both the 295- and 150-volt curves represent contributions from both the surface layer of atoms as well as atoms in the bulk. The 150-volt curve is, however, determined to a larger extent by the effect of the surface atoms. The resulant lower Debye temperature indicates a larger vibrational amplitude for the surface atoms. It is necessary to determine the magnitude of the attenuation of the incident beam before accurate values of the vibrational amplitude of the surface atoms can be calculated from these data. The vibrational amplitude of the surface atoms could presumably be determined directly from similar measurements on diffraction beams originating from surface atoms only. Such beams include those due to the displacement of the surface atoms from their normally expected position.

The nonlinear portion of these curves at the higher temperatures may possibly be due to the anharmonic nature of the vibrations of the surface atoms. The spacing of these atoms normal to the surface is increased by about 5% over the spacing of similar atoms in the bulk of the crystal.[3]

It is also possible to make similar measurements on the diffraction beams arising from a monolayer of adsorbed gas. In some cases the decrease in the intensity with increasing temperature is much more rapid for these beams than for the beams from the clean surface.

---

*Now at Cornell University, Ithaca, New York.

[1]J. A. Rayne and W. G. Kemp, Phil. Mag. 1, 918 (1956).

[2]M. Blackman, Handbuch der Physik, edited by S. Flügge (Springer-Verlag, Berlin, 1955), Vol. 7, p. 325.

[3]A. U. MacRae and L. H. Germer, Ann. N. Y. Acad. Sci. (to be published).

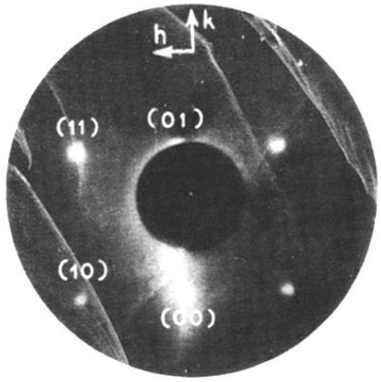

FIG. 1. Diffraction pattern of 130-volt (1.07 Å) electrons from the (110) surface of a clean nickel crystal at room temperature. The measurements in this paper are on the 01 beam, which is slightly obscured by a shield in this picture.