ductors of sufficient purity to observe isolated donor transitions), one can expect to find mass variations of the type reported here in the Zeeman spectra of other semiconductors. Thus, caution must be exercised in deducing accurate conduction-band masses from Zeeman splittings of donors in weak magnetic fields.

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Surface Molecular-Orbital Excitations in Electron Energy-Loss Spectra

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We have observed electronic transitions characteristic of molecules at a Ni(110) surface in the energy-loss spectra of 60- to 80-eV primary electrons. We present spectra of a clean Ni(110) surface, an unordered adlayer of nitrogen on Ni(110), and an ordered adlayer of sulfur in the Ni(110)-$c(2\times2)$S surface structure. These spectra derive from a two-step electron backscattering process involving an inelastic loss and an elastic scattering event at the crystal surface. The loss spectra of an ordered surface differ from those of a disordered surface in their sensitivity to primary-beam energy.

Several techniques have been used to study electronic energy levels of bonding electrons in impurities chemisorbed on a metal surface. Hagstrum and Becker[1] have developed the technique of ion neutralization spectroscopy (INS) with which they determined energy levels of chalcogenides on nickel surfaces. Eastman[2] and Waclawski and Plummer[3] reported photoemission spectra of impurities chemisorbed on different transition metals. Plummer and Young[4] determined energy spectra of alkaline-earth atoms adsorbed on tungsten surfaces by measuring the energy distribution of field-emitted electrons, and the authors of Ref. 3 used this last method to determine energy spectra of oxygen on tungsten.

In this paper, we report on the first observation of electronic energy levels of nitrogen and sulfur chemisorbed on a Ni(110) surface by the technique of electron energy-loss spectroscopy. In this spectroscopy, electrons undergo both an inelastic and an elastic scattering process at the crystal surface. Disordered adlayers produce diffuse elastic backscattering which changes weakly in intensity with primary energy [e.g., N on Ni(110)], whereas ordered adlayers produce diffractive elastic scattering which varies strongly with energy [e.g., $c(2\times2)$S on Ni(110)]. The energy dependence of the elastic scattering process is responsible for enhancement or suppression of particular loss structure in the spectra. The concept of energy loss coupled with diffraction has also been studied in the context of plasmon excitation.[5]

Measurements were made in two different low-energy electron-diffraction/Auger-electron spectroscopy (LEED/AES) systems in which the now common technique of using the LEED optics as a retarding potential analyzer was employed.[6] Both systems yielded similar results. The data shown are $dN(E)/dE$ curves in the energy range within 20 eV of the elastic peak of the secondary electron emission spectrum $N(E)$. Curves for different primary beam energies have been shifted so as to produce a common energy-loss abscissa. The $dN(E)/dE$ curves were taken with 1 or 2 V peak-to-peak ac modulation. Near-normal incidence of the primary beam was selected ($\theta \sim 3°$).

The nickel crystals were cleaned *in situ* using repeated heating, argon-ion bombardment, and oxidation treatments.[7] Surface conditions were assayed by LEED and AES. The specimen was held at 320°C for measurements of the clean surface, at room temperature for the nitrogen-covered surface, and at 220°C for the sulfur-covered surface. The vacuum was 1×10^{-10} Torr during measurements. The nickel surface was changed from the clean to the impurity-covered conditions several times, and the reproducibility of the energy-loss spectra was clearly demonstrated.

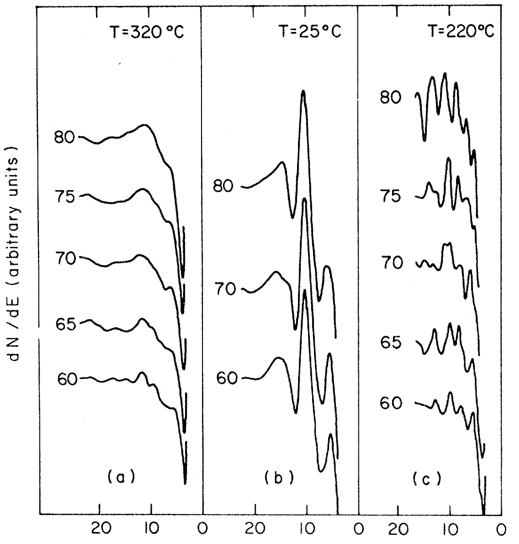

FIG. 1. Energy-loss spectra of electrons backscattered from a Ni(110) surface. Primary beam energies in eV are indicated on each curve. The surface conditions and modulation voltages are as follows: (a) clean surface, 2 V; (b) disordered nitrogen coverage, 2 V; (c) ordered sulfur coverage, $c(2\times2)$S, 1 V.

In Fig. 1(a) we show that the energy-loss spectra of a clean, ordered Ni(110) surface are nearly structureless and relatively insensitive to primary beam energy. The results with nitrogen adsorption are shown in Fig. 1(b). The nitrogen coverage was sufficiently disordered to create no new LEED structure and sufficiently dense to obliterate most of the clean (1×1)Ni pattern. Consequently, only diffuse scattering results. Note that the characteristic loss spectra of this disordered surface structure are insensitive to changes in primary beam energy as well as being distinctly different from the clean-surface spectra. The instrumental sensitivity used to obtain all the spectra of Fig. 1 was constant within 2%.

Shown in Fig. 1(c) are loss spectra characteristic of sulfur in the ordered Ni(110)-$c(2\times2)$S structure.[7] Features in these spectra clearly differ in number, energy position, and dependence on primary beam energy from the adsorbed nitrogen spectra.

The strong sensitivity of spectral features to primary beam energy, in the case of the $c(2\times2)$S surface, is a direct consequence of the influence of elastic scattering from an ordered surface structure. These modulation effects can be understood by emphasizing both steps of the two-step back-scattering process in the following way. It is assumed that the inelastic-loss step is governed by a discrete set of fixed energy losses. The elastic-scattering step provides propagation channels at those energies for which the diffraction conditions are satisfied. Thus when diffraction conditions are coupled with the loss step, before or after the loss event, enhancement of the spectra occurs at select energies. Considerable evidence persists in the $c(2\times2)$S loss spectra to support this point of view. The many observations that have been made can be summarized as involving a correlation between modulation of amplitudes in loss spectra with the I-V structure in individual Bragg beams and with the I-V structure of the net elastic current reaching the analyzer.[8]

The question of order in the two-step process (i.e., loss before[9] or after[10] diffraction) has been considered. Various features of the data support one or the other order. Neither order appears to be preferred in the analysis carried out thus far.

Only energy lost by an electron is observed.

Therefore no *a priori* identification of energy levels can be made on an absolute scale. It is necessary, consequently, to rely on other experimental evidence for a key to energy-level assignments. In principle, excited states and ionized states are accessible in this spectroscopy. Line-shape considerations incorporating an appropriate deconvolution scheme are prerequisite to a detailed analysis of these spectra.[8] In Fig. 2 we present a listing of the most prominent transitions that have been observed consistently, along with tentative energy-level diagrams.

The adsorbed nitrogen spectrum shows three transitions: 4.5, 8.0, and 11.2 eV. If we assume that the nature of the bonding in the adsorbed state is such that the Ni *d* band is not completely depleted of electrons, we find a simple interpretation of these three transitions by assigning the smaller value to a transition from the residual *d* band to a bound excited state. Since the *d* band lies approximately 1 eV below the Fermi level, this places the excited state 3.5 eV above the Fermi level. We then take the higher transition energy as indicative of a low-lying molecular orbital, as shown in Fig. 2, having an energy approximately 7.5 eV below the Fermi level. A value of the work function for the nitrogen-covered surface is needed to assign absolute values to these energy levels.

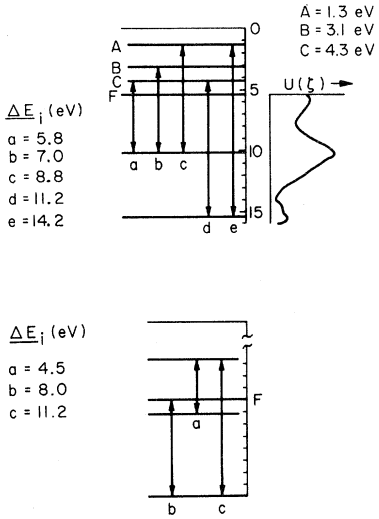

FIG. 2. Energy-level diagram of molecular orbitals characteristic of sulfur and nitrogen on a Ni(110) surface. These diagrams were constructed from the most pronounced transitions found in the energy-loss spectra. Upper diagram: energy levels for the Ni(110)-$c(2\times2)$S surface based upon transitions observed in INS in which two low-lying orbitals have been observed. The transition density $U(\zeta)$ from INS is plotted to the right. The energy scale was based on a work-function value of 5.29 eV. Lower diagram: energy levels for the disordered nitrogen coverage of a Ni(110) surface. Energy values are relative to the Fermi level (F) with 1-eV increments indicated.

The most prominent features of the $c(2\times2)$S surface are indicative of transitions at 5.8, 7.0, 8.8, 11.2, and 14.2 eV. These transitions can be fitted to an energy-level diagram having two occupied states below the Fermi level and three unoccupied states between the Fermi level and the vacuum zero. Such a configuration is compatible with the transition density as measured by Becker and Hagstrum for the Ni(110)-$c(2\times2)$S surface structure.[11] The energy-level diagram is shown in Fig. 2 along with the corresponding transition density $U(\zeta)$ obtained from INS. A work-function value of 5.29 eV was used.[11] In this interpretation the observed transitions arise as excitations from two occupied molecular orbitals of surface molecules to three excited states lying at 1.3, 3.1, and 4.3 eV below the vacuum zero.

Energy losses at 8.1 and 19.1 eV have been reported as excitations of surface and bulk plasmons in Ni.[12] For primary energies above 100 eV, we observe both losses clearly. The energy-loss spectra of the clean surface, Fig. 1(a), suggest a loss of 8 eV with a width of ~3 eV, consistent with the energy and linewidth reported for the surface plasmon in Ni. The 8.0-eV loss of the N-covered Ni surface is close to the reported surface-plasmon energy. The loss amplitudes of all three losses of Fig. 1(b) scale closely with nitrogen coverage as determined by AES, and at low coverage the 8.0-eV N line splits into two closely spaced lines with $\leqslant 1$ eV linewidth (typical of surface molecular excitations).[1] In view of these differences we believe that we have correctly distinguished between surface-plasmon excitations and molecular-orbital excitations.

We wish to acknowledge helpful discussions with Dr. L. C. Davis and Dr. W. L. Winterbottom.

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Low-Temperature Electromagnetic Generation of Ultrasound in Potassium*

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The magnetic field dependence of electromagnetic generation of 9.4-MHz ultrasound in potassium below 4.2°K has been measured and compared with calculations based upon a free-electron model of the metal. It is found that substantial differences exist between the experimental results and predictions of the theory.

Within the last few years, it has been realized that the response of a metal to an incident high-frequency electromagnetic field must include the ion motion within the skin depth. The electromagnetic fields produce an ultrasonic wave which propagates away from the surface.[1] In the limit of local electrical conduction, a steady magnetic field must be applied if measurable ultrasonic amplitudes are to be produced. The generation of the ultrasonic wave is, in this case, simply a manifestation of the Lorentz force acting on the induced currents.[2] However, under conditions of nonlocal conduction, appreciable coupling of the incident fields to the ions exists in the absence of an external magnetic field. These purely electromagnetic means of producing ultrasonic waves in conducting materials are referred to as electromagnetic generation.

Electromagnetic generation at megahertz frequencies in the absence of a steady magnetic field was first[3] observed in W and later[4] in Ag and Al, all metals with reasonably complex electronic structures. Because of this, it was not altogether surprising that experimental observations differed somewhat from predictions based upon a free-electron theory.

In an attempt to avoid possible complications arising from real-metal effects, it was decided to pursue experiments on potassium which has a nearly spherical Fermi surface. In this Letter, we report measurements of the magnetic field dependence of the electromagnetic generation of 9.4-MHz transverse ultrasonic waves in a single crystal of potassium having flat, parallel surfaces, and we compare these experimental results with calculations based upon a free-electron theory.[5] Although there are some areas of agreement, there appear to exist important differences between this theory and our experimental results. Furthermore, our observations are not consistent with conclusions drawn from other recent measurements of electromagnetic generation in potassium.[6] The degree of our differences with previous observations is difficult to assess because measurements at sufficiently low fields were not reported.

The (110) axis was chosen as the propagation direction since the large ratio of the two shear velocities (~1.8:0.7) prevents significant rotation of the plane of polarization in the *bulk* of the sample. This geometry has the further advantage that stray coupling to the slow shear mode [polarization parallel to $(1\bar{1}0)$] is easily recognized in this ultrasonic pulse-echo experiment as a second set of echoes with a distinct separation in time. Our measurements consisted of determining the amplitude of the fast shear wave generated by the rf fields for each of two orthogonal angular positions of the coil. These positions were determined to within 1° from the location of null positions in the rotation pattern. The measured field dependence of the ultrasonic ampli-