lent noise temperature T_e for T in Eq. (2) is justified. The question can be approached as follows: For particles of any given energy, mean square current fluctuations are easily obtained by assuming that the directions are randomly oriented. The T_e which can be calculated is related to the energy in exactly the same way as average energy and temperature of a Maxwellian, i.e., $E=\frac{3}{2}kT_e$. This is readily extended to $\bar{E}=\frac{3}{2}kT_e$ for an arbitrary distribution by assuming a collision frequency ν_0 independent of particle energy. The collision frequency enters because it is the reciprocal of the coherence time for the current fluctuations and therefore determines the bandwidth over which the fluctuations are spread. To what extent a collision frequency depending on velocity will cause deviation from $\bar{E}=\frac{3}{2}kT_e$ has not been resolved, but it is probable that the deviation will be very small. In either case, Maxwellian or otherwise, the use of $\bar{E}=\frac{3}{2}kT_e$ must be coupled with an assumption that recombination occurs with a probability independent of energy, so that Eq. (2) cannot be said to be an exact expression in either case. The other assumption, of an energy loss proportional to $T-T_0$, can also be replaced by a term T_e-T_0 with approximately as much justification.

It will be of interest to extend this work to a material for which the range of power for which observations can be made bridges the gap between very short equilibration time where the distribution is surely Maxwellian and the situation existing in the reported work. In the meantime it appears secure to regard this work as a valid measurement of $\tau_L/\tau_R=0.135$, at the temperature $T=35°K$.

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[1]E.g., F. R. Arams, E. W. Sard, B. J. Peyton, and F. P. Pace, IEEE J. Quantum Electron. 3, 484 (1967).

[2]S. M. Sze, *Physics of Semiconductor Devices* (Interscience, New York, 1969), p. 30, Fig. 12.

[3]L. Spitzer, Jr., *Physics of Fully Ionized Gases* (Interscience, New York, 1962), 2nd ed., p. 132, Eq. (5-25).

[4]By its manufacturer, Santa Barbara Research Corporation.

[5]S. M. Sze, *Physics of Semiconductor Devices* (Interscience, New York, 1962), p. 20, Table 2.2.

Observation of Surface-State Resonances in Low-Energy Electron-Diffraction Rotation Diagrams for Al

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Experimental study of low-energy electron-diffraction rotation diagrams from the (001) surface of Al reveals the appearance of systematic structure in the specularly reflected beam. This structure does not seem to be associated either with the secondary Bragg features or with the threshold effect. It has been identified as being due to the coupling between an incident beam and a localized surface state. A simple calculation of the φ dependence of the resonance minima based on the Kronig-Penney model confirms this conclusion. The resonance intensity profile is generally in agreement with McRae's prediction.

The subject of surface resonances has been first discussed in connection with low-energy electron diffraction (LEED) by McRae,[1] and since then it has been dealt with by several authors.[2-5] Among many types of resonances[6] particularly interesting from the experimental and theoretical points of view are the surface-wave (threshold-effect) and surface-state resonances. The threshold effect corresponds to the condition when a diffracted beam emerges just parallel to the surface of the crystal, i.e., when $k_{\perp,hk}^2=E-|\vec{k}_{\parallel}^{\,\mathrm{inc}}+\vec{g}_{hk}|^2=0$, where E is the incident energy and $\vec{g}_{hk}$ is a two-dimensional reciprocal-lattice vector associated with the (hk) beam. Dynamical model calculations usually show some structure at the threshold energy, but there has been some difficulty in trying to identify it experimentally. A resonancelike structure has been recently observed in the curves of intensity versus energy for the (001) surface of copper by Anderson.[7]

Another type of surface resonance has been discussed in connection with LEED in Refs. 3–5 and in connection with the scattering of atomic beams by Cabrera *et al.*[8] Here, the resonance minima[3] in the specular reflectivity are explained in terms of coupling between the incident beam and a localized surface state via a nonzero reciprocal-lattice vector. The incident beam gets scattered by a reciprocal-lattice vector $\vec{g}_{hk}$, and if the (hk) beam cannot exist outside the crystal $(k_{\perp,hk}^2 < 0)$, it is possible for the incident beam to become directly coupled to a surface state, losing some of the electrons to this state and thus causing minima in the specular reflectivity. These minima, which occur on the low-energy side of the emergence condition of the nonspecular beam, have been predicted and associated directly with surface states by Hirabayashi.[3] His treatment (exemplified by a Kronig-Penney model calculation) involved the intrinsic surface states which are due to the disruption of the periodic crystal potential by a surface. The finite crystal was assumed to consist of similar layers with identical scattering properties.

More extensive treatments of surface-state resonances have been carried out by McRae[4] (with a subsequent model calculation by Jennings[5]) and Cabrera *et al.*[8] Cabrera's discussion concerned the scattering of atoms which do not penetrate into the crystal beyond the first surface layer, and consequently the deeper-lying layers (substrate) have no effect on the intensities of the reflected beams. While his general treatment may be modified to include the case of electron scattering, one clearly cannot draw any direct comparison between the type of resonance profiles observed in atomic and electron scattering.

An important discussion of the effect of surface-state resonances on LEED intensity-versus-energy curves has been given by McRae.[4] His multiple-scattering analysis treated separately the effects of a surface layer (selvedge) and the rest of the crystal (substrate). The resonance structure was found to occur below the emergence threshold of the nonspecular beam, and the resulting amplitude reflectivity of the specular beam was found to be given by

$$A_{00} = C\left(1 + R\frac{\frac{1}{2}\Gamma}{E - E_0 + i\frac{1}{2}\Gamma}\right),$$

where C is the background amplitude, R is the ratio (complex) of the resonance to background amplitudes, E is the incident energy, Γ is the width, and E_0 is the position of the resonance. Thus, the total amplitude is the superposition of the potential scattering term (which gives the background) and the resonance scattering term which is of the Breit-Wigner form. This result is expected to apply well at low energies, below the first inelastic excitation threshold. The resonance width in this case is of the order of 1–2 eV. At higher energies one expects deviations from the Breit-Wigner result and an order-of-magnitude increase in the resonance width. The actual resonance profile is a sensitive function of R and may appear as a maximum, minimum, or a combination of the two.

Jennings[5] has examined the importance of the shape and position of a surface barrier on the resonance profiles. His calculations, performed for square and image potential barriers, demonstrated the sensitivity of the resonance structure on the barrier parameters and confirmed the theoretical predictions of McRae.

Let us note that discussion of the surface-state resonance was always limited to its effect on the curves of intensity versus energy, where it constitutes a very minor feature, lost among the more prominent primary and secondary Bragg peaks (except perhaps at the energies below ~13 eV). In the typical I-vs-E LEED experiments performed with conventional equipment, an unambiguous experimental observation and identification of the structure associated with the surface-state resonance is rather difficult.

In the present Letter we would like to report some of our experimental results obtained for the (001) surface of Al. We have performed a series of experiments recording the I-vs-φ spectra for constant E and θ (rotation diagrams), where E is the incident energy and θ and φ are the polar and azimuthal angles of the incident beam, respectively. The measurements were always taken at $E = 20$ eV, for θ between 32° and 76° in steps of 4° and φ between 0° and 45°, using our new goniometer apparatus[9] which provides for an automatic recording of the $I_{00}(\varphi)$ spectra. The angular resolution of the goniometer is about 0.1°. Figure 1 shows two such experimental rotation diagrams for different angles θ. We note that each curve clearly exhibits a resonance structure. Furthermore, this structure always occurs well before the emergence condition of the $(\bar{1}\bar{1})$ beam and has the general profile predicted by McRae. An insert in this figure shows a detailed angular profile of the resonance, which was obtained by subtracting a (nonconstant) back-

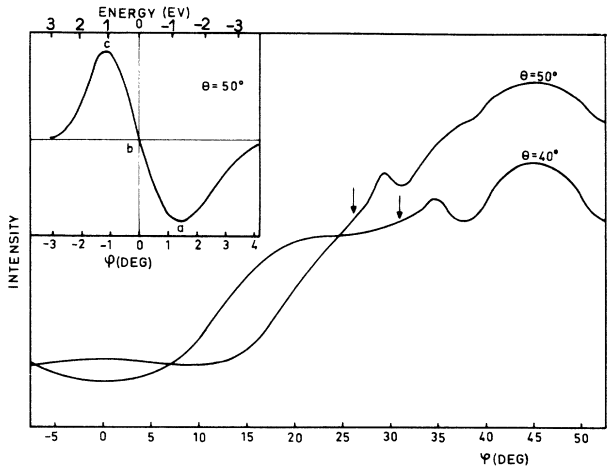

FIG. 1. Experimental (00) beam rotation diagrams at $E=20$ eV for $\theta=40°$ and $\theta=50°$. The arrows indicate the emergence angles of the $(\bar{1}\bar{1})$ beam. Insert in the upper left-hand corner shows an expanded profile of the resonance with both angular (bottom) and energy (top) scales. Points a, b, and c denote the minimum, inflection point, and maximum of the resonance, respectively.

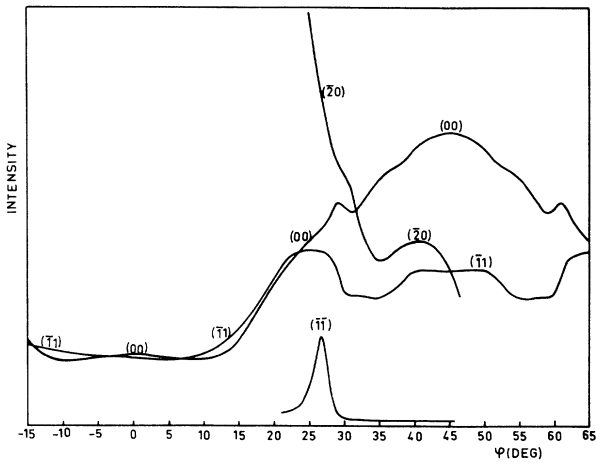

FIG. 2. Summary of the experimental results at $E=20$ eV, $\theta=50°$. All beams are plotted on the same angular scale. Intensity scale for the $(\bar{2}0)$ beam is 10 times larger than that of the $(\bar{1}\bar{1})$ and $(1\bar{1})$ beams. Intensity profile for the $(\bar{1}\bar{1})$ beam was obtained with the photometer set at a constant angle $\theta=90°$; maximum in this profile corresponds to the appearance of $(\bar{1}\bar{1})$ beam.

ground from the global $I_{00}(\varphi)$ curve. This background over the resonance region was obtained by extrapolating the behavior of the curve of I_{00} vs φ in the absence of the resonance. We see that the angular width of the resonance is of the order of 7°, which corresponds to an energy spread of 6.3 eV, as measured from the emergence threshold. The same type of structure, but much weaker, is also present in the nonspecular beams which exist outside the crystal at 20 eV, as is illustrated on Fig. 2. This figure also shows the emergence of the $(\bar{1}\bar{1})$ beam plotted on the same angular scale as the specular beam. We see that indeed the $(\bar{1}\bar{1})$ beam appears after the resonance structure in the (00) beam, thus eliminating a possible objection that this angular difference is due to the uncertainty in energy [an increase in energy of 1.5 eV shifts the emergence threshold at $\theta=50°$ from $\varphi=24.8°$ (at $E=20$ eV) to $\varphi=26.8°$ (at $E=21.5$ eV)].

The emergence angle of the $(\bar{1}\bar{1})$ beam was obtained by setting a photometer with a small circular aperture (~0.3 mm in diameter) at $\theta=90°$, i.e., just parallel to the crystal surface. Once the beam has passed through the photometer aperture, the recorded intensity drops. In this way we can accurately determine the emergence angle. The uncertainty in θ introduced by the aperture size is of the order of 0.3°, which is of no consequence. The experimental emergence angles determined in this manner were found to be in exact agreement with the calculated threshold angles (K II line) provided we took the incident energy to be 20.8 eV instead of 20.0 eV. This correction of 0.8 eV due to the contact potential is identical to the one determined in a different way—by measuring the diffraction angles of nonspecular beams at normal incidence.

Figure 3 shows the summary of the experimen-

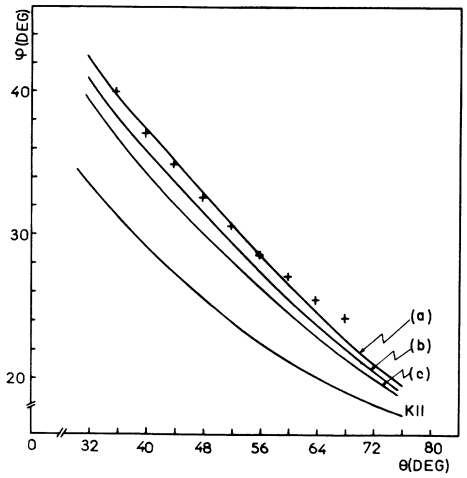

FIG. 3. Plots of the minima (curve a), inflection points (curve b), and maxima (curve c) of the resonance; K II line which represents the emergence thresholds of the $(\bar{1}\bar{1})$ beam is also given for comparison; calculated positions of the surface states are denoted by crosses.

tal results. This is a plot of the values of θ and φ for which one observes a minimum in the specular reflectivity (curve *a*), the inflection point (curve *b*), and a maximum (curve *c*). The *K* II line[10] also plotted on this figure gives the threshold values of θ and φ corresponding to the emergence of ($\bar{1}\bar{1}$) beam.

This systematic appearance of resonance structure may be understood on the basis of simple arguments involving coupling between the incident field and a surface state. Following Hirabayashi[3] we assume that the total wave field inside the crystal may be represented as a set of weakly coupled resonating states ψ_{hk} corresponding to each (hk) beam. These states satisfy the uncoupled Schrödinger equation

$$\left[-\frac{\hbar^2}{2m}\frac{d^2}{dz^2}+V_0(z)\right]\psi_{hk}(z)=E_{\perp,hk}\psi_{hk}(z),$$

where $E_{\perp,hk}=k_{\perp,hk}^2$ as has been defined above and $V_0(z)$ is the crystal potential in the z direction averaged over the surface. We note that the bound solutions of this equation are possible when $E_{\perp,hk}<0$ which can only happen if $\tilde{g}_{hk}=0$. We take the Kronig-Penney potential for $V_0(z)$ with a well width equal to αd, cell width equal to d, and a well depth equal to $-V_0/\alpha$. The crystal surfaces are taken to be at $z=0$ and $z=Nd$. Using the Bloch theorem and matching the cell solutions at the cell boundaries as well as to the exponentially decreasing solutions outside the left and right surfaces, we obtain the following condition for the existence of surface states[11]:

$$\cos(k_1\alpha d)=\cosh(kd)\cosh[\varkappa_1 d(1-\alpha)]+\sinh(kd)\coth(kNd)\sinh[\varkappa_1 d(1-\alpha)],$$

where

$$k_1^2=(2m/\hbar^2)[E_{\perp,hk}+V_0/\alpha]$$

and

$$\varkappa_1^2=(2m/\hbar^2)|E_{\perp,hk}|.$$

In the limit as $N\to\infty$ the above equations reduce to

$$E_{\perp,hk}=-\frac{V_0}{\alpha}+\frac{\hbar^2}{2m}\left(\frac{2n\pi}{\alpha d}\right)^2.$$

This equation is satisfied only for certain angles θ and φ which give the condition of coupling into the surface states. The calculations were performed using the following values for the parameters: $d=4.04$ Å, $V_0=18.6$ eV, and $\alpha=0.52$. The results are shown in Fig. 3. We see that between $\theta=36°$ and $\theta=64°$ the positions of the resonance minima correlate well with the positions of the surface states. The discrepancy becomes more apparent at higher values of θ. Thus, we see that systematic structure of the type observed experimentally can be already expected on the basis of a highly simplified model involving constant-energy, θ-independent surface states. In fact, the experimentally deduced surface-state energies exhibit a pronounced θ dependence.

In conclusion, we have observed a systematic resonance structure in the $I_{00}(\varphi)$ profiles which can be explained in terms of resonance involving surface states. Sample calculations with the Kronig-Penney model confirm this explanation. Resonance profiles exhibit the general shape predicted by McRae. Detailed dynamical calculations of the resonance using dynamical theory are presently in progress and will be reported elsewhere.

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[1]E. G. McRae, J. Chem. Phys. 45, 3258 (1966).
[2]D. S. Boudreaux and V. Heine, Surface Sci. 8, 426 (1967).
[3]K. Hirabayashi, J. Phys. Soc. Jap. 25, 856 (1968).
[4]E. G. McRae, Surface Sci. 25, 491 (1971).
[5]P. J. Jennings, Surface Sci. 25, 513 (1971).
[6]K. Kambe, to be published.
[7]S. Andersson, Surface Sci. 19, 21 (1970).
[8]N. Cabrera, V. Celli, F. O. Goodman, and R. Manson, Surface Sci. 19, 67 (1970).
[9]L. De Bersuder, in *Proceedings of the Seventh International Conference on Electron Microscopy, Grenoble* (Societé Francais de Microscopie Electronique, Paris, 1970), p. 147.
[10]L. De Bersuder, C. R. Acad. Sci., Ser. B 266, 1489 (1968).
[11]It must be noted that Eq. (29) in Ref. 3 is incorrect and while the physical conclusions remain unchanged, the actual form of the subsequent equations, particularly Eq. (30), must be modified.