geneous. We believe that the inhomogeneities are due to local strains introduced by the cleavage and that these strains are annealed at room temperature over a period exceeding 1 day. It is not reasonable to attribute these changes to adsorption of residual gases because (1) the sticking probability of gases on cleaved III-V surfaces was found to be extremely small,<sup>6</sup> (2) it would seem improbable that contamination would homogenize the band bending in two different cases, and (3) the ionization energy is not changed.

While the above described behavior is most conspicuously displayed by GaSb, it is not restricted to this substance. We have found inhomogeneous work function and band bending in *n*-type GaAs.<sup>4</sup> In this case, however, no annealing was observed when the crystals were kept at room temperature. On cleaved InP surfaces,<sup>7</sup> we observed unreproducible surface potential and surface-charge densities. Thus, this behavior seems quite general.

In connection with the concept of surface states, it is interesting to note that "annealing" increases the band bending and surface charge and also that samples with flat bands, i.e., p-type bulk in both GaSb<sup>8</sup> and GaAs<sup>4</sup>, do not present the spatial or the temporal variations discussed above. Thus it seems that the effect of strains is to reduce the surface states or shift them towards the conduction band.

The fact that annealing occurs at room temperature for GaSb suggests that clean, well-defined surfaces with well-known doping and stoichiometry can probably be achieved by cleaving and heating to temperatures well below those that would cause appreciable diffusion of impurities or decomposition of the material.

\*Work supported by the Night Vision Laboratory, Fort Belvoir, Va. under Contract No. DAAK 022-68-C-0232, and by the Connecticut Research Commission under Contract No. RSA-69-7.

<sup>†</sup>Permanent address: University of the Orange Free State, Bloemfontein, Republic of South Africa.

 $^{1}$ G. A. Barnes and P. C. Banbury, Proc. Phys. Soc., London <u>71</u>, 1020 (1958); G. W. Gobeli and F. G. Allen, J. Phys. Chem. Solids <u>14</u>, 23 (1960).

<sup>2</sup>J. J. Lander, G. W. Gobeli, and J. Morrison, J. Appl. Phys. 34, 2298 (1963).

<sup>3</sup>D. R. Frankl, J. Appl. Phys. 34, 3514 (1963).

<sup>4</sup>J. H. Dinan, L. K. Galbraith, and T. E. Fischer, to be published.

<sup>5</sup>T. E. Fischer, Surface Sci. <u>13</u>, 30 (1969).

<sup>6</sup>A. U. MacRae and G. W. Gobeli, J. Appl. Phys. <u>35</u>, 1629 (1964).

<sup>7</sup>T. E. Fischer, Helv. Phys. Acta 41, 827 (1968).

<sup>8</sup>P. E. Viljoen and T. E. Fischer, in Proceedings of the Thirty-First Conference on Physical Electronics, Gaithersburg, Virginia, March 1971 (to be published).

## Angular Distribution of Photoelectrons Emitted from Copper Single Crystals\*

U. Gerhardt and E. Dietz

Physikalisches Institut der Universität, Frankfurt am Main, Germany (Received 23 April 1971)

We measured the energy distribution of electrons emitted from a copper single crystal at 60° to the surface normal, using plane polarized light at normal incidence in the near uv region. Rotating the plane of polarization produced changes in the electron distribution between 5 and 28%. No such changes could be detected upon substituting a polycrystalline sample. The energy distribution of the single crystal differs considerably from that of the polycrystal. The results imply direct, k-conserving transitions and no scattering for a large fraction of those excited electrons which leave the crystal.

Ever since Gobeli, Allen, and Kane<sup>1</sup> published their pioneering work on the directional dependence of the photoemissive yield of Ge and Si crystals, the importance of similar measurement for other materials was emphasized.<sup>2</sup> The only other experimental information on the subject is obtained from photoemission electron microscopy.<sup>3</sup> In this Letter we present the energy distribution of electrons emitted from a Cu crystal and a polycrystalline Cu film for different directions of observation and different polarization and energies of the incident radiation. Furthermore, we discuss the implications of the results for the excitation and emission process.

The experimental setup is shown schematically in Fig. 1 which is drawn roughly to scale. It also indicates the orientation of the crystal. The surface of the single crystal was prepared by



FIG. 1. The experimental arrangement for investigation of the angular distribution of photoelectrons. The drawing is essentially in correct scale. The radius of the Cu hemisphere is 20 mm. The orientation of the single crystal is also indicated. The two observation directions are denoted by A and B.

mechanical grinding and polishing to the proper orientation, annealing in a hydrogen atmosphere at about 700°C, and electropolishing with orthophosphoric acid. The crystal was then quickly transferred to the vacuum chamber and annealed by the heater indicated in Fig. 1. The vacuum employed was in the 10<sup>-9</sup>-Torr range. The magnetic field in the neighborhood of the sample was below 0.05 G. The full width at half-maximum of the uv radiation, produced by a hydrogen discharge and a grating monochromator, was 0.13 eV. The channel electron multipliers were made in our laboratory. Their output pulses were stored in different channels of a multichannel analyzer. The dwell time on one channel was 0.32 sec, while the retarding voltage was increased linearly from zero to its maximum value within 30 sec. A full cycle for one detector consisted of two sweeps for the two polarizations of the radiation indicated in Fig. 1. In a typical measurement, which took about 8 h,  $10^5$  counts were accumulated in one channel for zero retarding voltage. After completion of the measurement, the spectra were differentiated and averaged in order to obtain the energy distribution.

The average energy distributions N(E) for  $\hbar\omega$ = 5.4 and 6.2 eV are given in the lower part of Fig. 2. The subscripts A and B refer to measurements with the detector in position A and B, respectively (Fig. 1). The energy distribution for the evaporated Cu film is denoted by  $N_F$ . The maximum of N(E) is normalized to the same value in all cases. The zero line for the three curves taken with  $\hbar\omega = 6.2$  eV is shifted upwards as indicated. The relative polarization  $\Delta$ , defined as  $(N_{\parallel}-N_{\perp})/N$  with  $N = (N_{\parallel}+N_{\perp})/2$ , is given in the upper part of Fig. 2. The symbols  $\parallel, \perp$  re-



FIG. 2. The average energy distributions N(E) (lower part) and relative polarization  $\Delta$  (upper part) for two photon energies. The subscripts A and B refer to the two detector positions as indicated in Fig. 1. The energy distribution for the evaporated Cu film is denoted by  $N_F$ . The maximum of N(E) is normalized to the same value in all cases; the zero line for the different excitation energies is displaced.

fer to the (110) plane, i.e., the plane of Fig. 1. Within the accuracy of our experiment, we could find no polarization effect for the Cu film, which means that  $\Delta_F$  is well below 1% for all photon and electron energies investigated.

We base the theoretical interpretation of our result on the assumption that direct, k-conserving transitions are the correct model for the excitation process. For the time being we consider only photoelectrons escaping from the crystal without scattering. The operator of the matrix element describing the interband transition is  $\hat{A} \cdot \hat{p}$ ,  $\hat{A}$  being the vector potential of the electromagnetic field. The form of the operator shows that the occupation of final states belonging to the different arms of the star of  $\tilde{k}$  is anisotropic. If we were to calculate optical constants for a cubic material, we would have to sum over the degenerate states and the anisotropy would vanish. This is not true for the case of photoemission: We must apply the proper boundary conditions to each excited state individually.

Figure 3 shows the energy contours of initial and final states relevant to our experiment.<sup>4</sup> We



FIG. 3. Energy contours of initial and final states of Cu. The plane of the figure is  $(1\overline{1}0)$ ; it contains the surface normal and the two detectors. The heavy line is the intersection of the Fermi surface with the  $(1\overline{1}0)$  plane. Another contour 1.2 eV below  $E_{\rm F}$  is also given. The ellipsoids centered at the *L* points correspond to final states with energies  $\Phi = 4.55$  eV and  $\Phi + 1.2$  eV = 5.75 eV above  $E_{\rm F}$ ,  $\Phi$  being the work function of Cu. The dashed lines parallel to the surface normal belong to  $E_{\rm vac}^2 = k_t^2/\sin^2 60^\circ$ .

can read off the photon energy of a transition with a particular k as the difference of final and initial states at the corresponding point of Fig. 3. The energy conservation for the emission process requires  $E = E_{\text{final}} - \Phi$ . The continuity of  $\Psi$ and its normal derivative at the boundary leads to the conservation of the component  $k_t$  of  $\mathbf{k}$  parallel to the surface.<sup>1</sup> Neglecting the finite angular resolution of our detectors, we conclude that the photoelectrons detected in our measurement originate from states with  $\bar{k}$  parallel to the (110) plane. The dashed lines in Fig. 3 belong to E $=k_{\rm vac}^2 = k_t^2 / \sin^2 60^\circ$ . Thus, photoelectrons detected in our experiment originate from points in k space where a dashed line and an ellipsoid belonging to the same value of E intersect. As an example, the k vector marked  $\hbar \omega = 5.9$  eV and E = 0.3 eV is shown: Photoelectrons excited by photons of that energy originate from the  $\Lambda$  axis parallel to [111]. They will be detected by the

multiplier in position A.

On the other hand, the points of intersection of the same set of ellipsoids with the dashed line of the appropriate energies which lie to the left of the normal all fall in the region enclosed by the dog's bone, i.e., the initial states are unoccupied and optical transitions forbidden. However, optical transitions are allowed at the points where the dashed lines intersect the ellipsoids centered at  $\left[\frac{1}{2}\frac{1}{2}\right] + [111]$  (in units of  $2\pi/a$ ). The k vector shown in Fig. 3 corresponds to photoelectrons which were excited by 6.2-eV photons; they show up at the detector in position *B* with a kinetic energy of 0.9 eV.

Turning to the polarization dependance, we note that the transition  $\Lambda_1 - \Lambda_1$  is only excited if  $\overline{A}$  has a component parallel to [111]. We therefore expect the relative polarization  $\Delta$  to be large and positive. For k vectors away from  $\Lambda$ but in the (110) plane, the selection rule is somewhat relaxed: No transitions are allowed for  $\overline{A}$ perpendicular to the (110) plane.

The experimental results shown in Fig. 2 support the predictions of the theory outlined above. The curves  $N_A(E)$  and  $N_B(E)$  are peaked at low energies because we are dealing with  $\hat{k}$  vectors close to the  $\Lambda$  axis where the initial states are lowest in energy. For the polycrystalline film, photoelectrons originating from  $\Lambda$  transitions are much less probable, thus shifting the peak in N(E) to higher energies. The relative polarization for the single crystal is indeed high and positive in sign. Its value is probably limited by the finite angular resolution of our detector and by the background of electrons which were scattered before escaping into the vacuum.

We remark that the mechanism which we propose to explain the measurement with the detector in position B is very similar to the situation encountered in low-energy electron-diffraction experiments, where the tangential component of the  $\bar{\mathbf{k}}$  vector of the incoming and outgoing electron wave differ by the tangential component of a reciprocal lattice vector. Much of the formalism developed to describe the low-energy electron-diffraction experiments should also be applicable to photoemission.

The strong polarization effects and the pronounced differences which we found between the directional energy distribution of the single crystal and that of the film do not support the model of nondirect transitions proposed by Spicer.<sup>5</sup> This model also failed to explain the experimental results of piezo-optical investigations of Cu

crystals.<sup>6</sup> It was realized that the relatively simple mathematical formalism used in the nondirect model might just be an approximate substitute for the more complex formula appropriate for direct transitions.<sup>7</sup> Later on, the photoemission of the noble metals was more often interpreted in terms of direct transitions. Most recently, Doniach<sup>9</sup> proposed a many-electron theory of nondirect transitions. If applicable, the effect of this mechanism would be to reduce the intensity of the k-conserving transitions. The more recent results on photoemission do not favor this interpretation.<sup>8</sup> One important assumption which enters into the theory proposed by Doniach is a large effective mass of the electrons in the initial states. The results reported in this Letter refer to transitions between s-pbands with strong d admixture. However, the photon energy was not high enough to excite electrons from the flat d bands themselves. We hope that it will be possible to determine quantitatively the relative importance of nondirect and direct transitions from experimental results on the directional photoemission in the vacuum-uv region, where transitions from the d bands are important for photoemission of clean Cu single crystals.

We have benefited from helpful discussions with Professor W. Martienssen, Dr. W. Mohler, Professor H. Thomas, and Professor J. Treusch. We are also indebted to Dr. W. Schönherr for growing the crystal used in our experiment.

\*A project of the Sonderforschungsbereich "Festkör-

perspektroskopie" Darmstadt-Frankfurt, financed by special funds of the Deutsche Forschungsgemeinschaft.

<sup>1</sup>G. W. Gobeli, F. G. Allen, and E. O. Kane, Phys. Rev. Lett. <u>12</u>, 94 (1964); E. O. Kane, Phys. Rev. Lett. <u>12</u>, 97 (1964).

<sup>2</sup>The application of the method to study the electronic structure of metals was discussed by H. Thomas, in *Basic Problems of Thin Film Physics, Proceedings of the International Symposium, Clausthal-Göttingen, September 1965,* edited by R. Niedermayer and H. Mayer (Vandenhoeck and Ruprecht, Göttingen, Germany, 1966), p. 307; and by G. D. Mahan, Phys. Rev. Lett. <u>24</u>, 1068 (1970).

<sup>3</sup>Different grains of a polycrystalline sample show large variations in contrast. Results on Cu were reported by Ch. Zaminer, in *Proceedings of the Fourth European Regional Conference on Electron Microscopy*, edited by D. S. Bocciarelli (Tipografisa Poliglotta Vaticana, Rome, Italy, 1968), Vol. I, p. 123. We are indebted to Dr. Schimmel for pointing out the connection with photoemission microscopy.

<sup>4</sup>The eigenvalues used in Fig. 3 were taken from Table III in G. A. Burdick, Phys. Rev. <u>129</u>, 138 (1963).

<sup>5</sup>W. E. Spicer, Phys. Rev. Lett. <u>11</u>, 243 (1963); C. N. Berglund and W. E. Spicer, Phys. Rev. <u>136</u>, A1030, A1044 (1964); W. E. Spicer, Phys. Rev. <u>154</u>, 385 (1967); W. F. Krolikowski and W. E. Spicer, Phys. Rev Rev. <u>185</u>, 882 (1969).

<sup>6</sup>U. Gerhardt, Phys. Rev. <u>172</u>, 651 (1968).

<sup>7</sup>U. Gerhardt, Bull. Amer. Phys. Soc. 13, 468 (1968).

<sup>8</sup>N. V. Smith, W. E. Spicer, Opt. Commun. <u>1</u>, 157 (1969); N. V. Smith, Phys. Rev. Lett. <u>23</u>, 1452 (1969); P. O. Nilsson, C. Norris, and L. Wallden, Solid State Commun. <u>7</u>, 1705 (1969); D. E. Eastman and J. K. Cashion, Phys. Rev. Lett. <u>24</u>, 310 (1970); N. V. Smith and M. M. Traum, Phys. Rev. Lett. <u>25</u>, 1017 (1970).

<sup>9</sup>S. Doniach, Phys. Rev. B <u>2</u>, 3898 (1970).

## Critical Magnetic Neutron Scattering from CoO

M. D. Rechtin and B. L. Averbach

Department of Metallurgy and Materials Science, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139 (Received 22 March 1971)

The critical magnetic neutron scattering from CoO has been measured near the Néel temperature  $T_{\rm N}$ . The diffuse intensity at various wave vectors was assumed proportional to  $A_+|T/T_{\rm N}-1|^{-\gamma}$  above  $T_{\rm N}$  and  $A_-|T/T_{\rm N}-1|^{-\gamma'}$  below  $T_{\rm N}$ . Using the method of Als-Nielsen, we measured the temperature dependence of the critical scattering at several values of q [the displacement from the (111) position in reciprocal space] and used these data to calculate the relative magnitudes of  $\gamma$  and  $\gamma'$ . In order to satisfy scaling law requirements we referred our measurements to a rigid lattice by correcting for the large tetragonal contraction below  $T_{\rm N}$ . We found that  $\gamma' = (1.02 \pm 0.02)\gamma$ , and this suggests that static scaling laws may apply to CoO. In addition we ascertained that  $A_+/A_- \cong 7.6 \pm 1.5$  in agreement with the linear theory of Schofield, where  $A_+/A_- = 6.0 \pm 0.8$  for CoO.

We have recently presented magnetic neutron scattering measurements of the long-range antiferromagnetic order in CoO near the Néel temperature.<sup>1</sup> The intensity of neutrons scattered by  $\text{Co}^{2+}$  ionic moments for the (111) magnetic peak varied as  $I \propto (T_N - T)^{2\beta}$  in the critical region,