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Photoelectric Emission from Zn*

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The quantum yield, energy distribution, and temperature dependence of photoelectric emission from the basal plane of single crystals of high-purity (99.999%) Zn have been measured. The quantum yield is temperature-dependent and is consistent with a free-electron model in which transitions are phonon-assisted. The change in shape of the energy distribution curves in going from $h\nu = 9.32$–9.54 eV is consistent with the onset of the plasma region rather than with the excitations from d states. The work function for the basal plane is 3.63 eV.

I. INTRODUCTION

Measurements of the basal plane reflectance of single crystals of high-purity Zn have shown that Zn is well described as a free-electron metal.[1] The reflectance is about 85% or higher for wavelengths greater than 1310 Å, but drops sharply at about 1310 Å, i.e., 9.46 eV. The sharp drop at 9.46 eV was taken to correspond to the free-electron plasma frequency. However, since the onset of transitions from d states is expected to take place at about 11 eV,[2] there was some ambiguity as to whether the drop in reflectance results from the optical properties of a free-electron metal above the plasma frequency or from d-state transitions. To resolve these ambiguities, we have made measurements of the quantum yield, energy distribution, and temperature dependence of photoelectric emission from Zn single crystals.

II. EXPERIMENTAL

Single crystals of Zn (99.999%) were cleaved along the basal plane in a vacuum chamber at pressures less than 10^{-9} Torr. The pressure was maintained at less than 10^{-9} Torr at all times except for the few minutes required for making an energy distribution measurement. Since the Vacion pump used requires a magnetic field for operation, it had to be turned off during these measurements to avoid any distortion. It is possible that a slight contamination of the cleaved crystal surface resulted from the need to turn the pump off and on. That the surfaces were nonetheless quite clean will be made clear in the discussion of experimental results. In any case, slight contamination is not a critical factor in discussing the main points we wish to make.

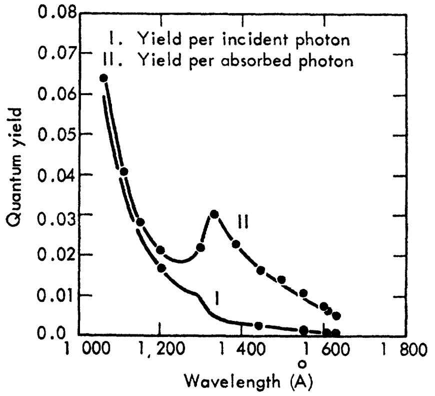

FIG. 1. Quantum yield versus λ.

The techniques used in the measurements of energy distributions and quantum yields were similar to those used by Berglund and Spicer.[3] Relative light intensities were measured using sodium-salicylate-coated phototubes.[4] A nitric oxide ionization chamber was used to measure the absolute light intensity at the Lyman-α wavelength (1216 Å). The spectral reflectance $R(\lambda)$ was measured previously on single crystals from the same batch.[1]

III. QUANTUM YIELD AND WORK FUNCTION

The quantum yield (electrons per photon), corrected for the absorption of the LiF window used in the vacuum chamber, is shown in Fig. 1. The work function for the basal plane of Zn was found from a Fowler plot[5] to be 3.63 eV (see Fig. 2).

Note that the quantum yield per incident photon increases sharply between 1320 and 1300 Å (Fig. 1). This is consistent with an onset of the plasma region at 1310 Å; the drop in reflectance at 1310 Å simply means more light is absorbed in the Zn.

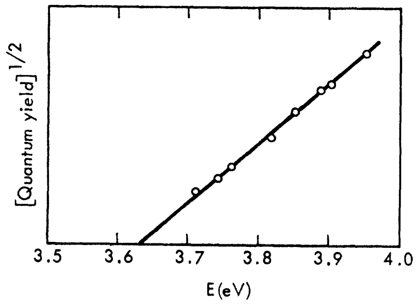

FIG. 2. Fowler plot for Zn.

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From the reflectance for Zn,[1] it is found that the total absorption increases by a factor of about 2.5 in going from 1320–1300 Å. A decrease by a factor of about 1.5 in the absorption coefficient, as calculated from optical data,[1] means an increase by a factor of 1.5 in the mean excitation depth. Because there is no significant change in such parameters as scattering cross sections for a change of only 20 Å in wavelength, we expect a relative increase in yield per incident photon of about 2.5/1.5, i.e., about 1.7. From Fig. 2 we see that this is obtained. Of course the decrease in absorption coefficient results in a corresponding decrease in the yield per absorbed photon.

IV. ENERGY DISTRIBUTION MEASUREMENTS

The results of a number of electron energy distribution measurements are presented in Figs. 3, 4, and 5. The scales are such that the area under a curve of $N(E)$ versus E equals the quantum yield (electrons emitted per photon absorbed). Also, the abscissa is shifted with respect to the vacuum level by subtracting the photon energy from the measured external kinetic energy. If energy losses from scattering are ignored, the energy along the abscissa is the energy corresponding to the initial state of the electron. When the energy distribution is referenced with respect to the initial states, any structure that may exist in the initial density of states is more apparent.

Figure 3 gives evidence of some structure in the initial density of states. The structure is weak and is not always resolved in all samples; however, when it does show up it is always at the same place. The structure is presumably related to structure at the points T and L in the Brillouin zone. Other points in the Brillouin zone are relatively unimportant in contributing to structure in the density of states. For example, K tends to be unimportant because the band gap at K is so small that it allows magnetic breakdown.[6] The point A can be ignored because only degenerate states exist there, and there is no band gap no matter how large the crystal potential.[7]

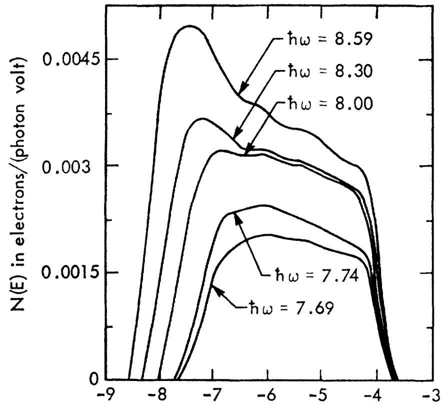

FIG. 3. Photoelectron energy distribution, $\hbar\omega=7.69\text{–}8.59$ eV.

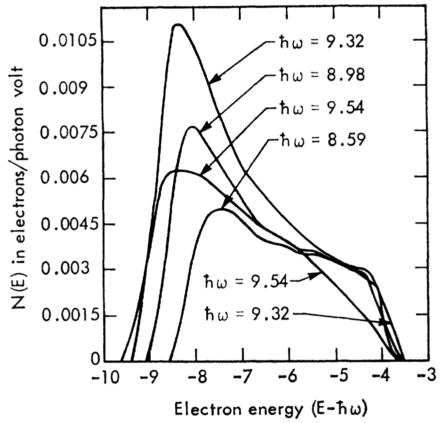

FIG. 4. Photoelectron energy distribution, $\hbar\omega=8.98\text{–}9.54$ eV.

It was noted previously that the quantum yield (electrons emitted per photon absorbed) decreases in going from $\lambda=1320\text{–}1300$ Å, the reason being that the absorption coefficient decreases and hence the mean excitation depth increases. An increase in the mean depth of escape at the onset of the plasma region is indicated by the rounding off of the high-energy knee in the energy distribution curve (see Fig. 4) in going from 1320–1300 Å (9.32–9.54 eV). The rounding off arises from a greater influence of scattering when the mean excitation depth is increased. The important point is that both the quantum yield and energy distribution curves support the view that the drop in reflectance of Zn at 9.46 eV corresponds to the onset of the plasma region. If transitions from d states were responsible for the decrease in reflectance, there would be no change in shape of the high-energy edge of the energy distribution curve in going from $h\nu=9.32\text{–}9.54$ eV. These high-energy electrons come from near the Fermi level.

That the cleaved-crystal surfaces were quite clean is indicated by the sharp high energy edge of the energy distribution curves shown in Figs. 3 and 4. Small amounts of surface contaminants generally destroy this sharp edge for free-electron metals.[8]

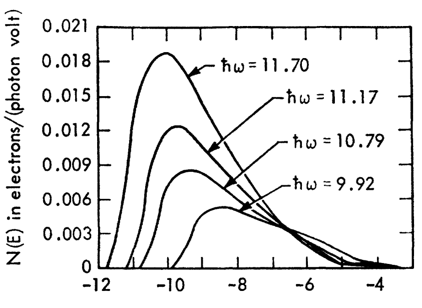

FIG. 5. Photoelectron energy distribution, $\hbar\omega=9.92\text{–}11.70$ eV.

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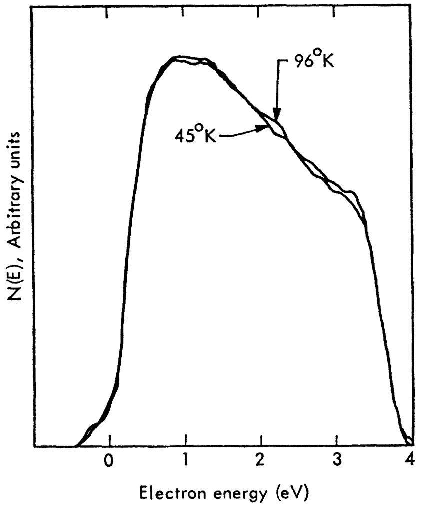

FIG. 6. Comparison of photoelectron energy distribution at 96°K with that at 45°K.

V. TEMPERATURE DEPENDENCE OF PHOTOEMISSION

The Zn crystal was mounted on the end of a Dewar protruding into the vacuum chamber. Both liquid nitrogen and liquid helium were used in the Dewar to cool the Zn crystal. Because it was not feasible to provide complete thermal shielding for the crystal, the equilibrium temperatures of the crystal were 96°K for liquid nitrogen and 45°K for helium. These coolants were used for two purposes: to cool the Zn crystal so that it could be easily cleaved, and to study the temperature dependence of photoemission.

The energy distribution curves measured at 96 and 45°K are nearly identical (see Fig. 6), but with the 96°K curve slightly above the 45°K curve. Figure 7 shows a comparison of the 96°K energy distribution curve with a room temperature (290°K) curve. To ensure that these three curves were normalized properly with respect to each other, they were recorded using the same sample, the same radiation intensity and wavelength (1612 Å), and the same electronic gain settings.

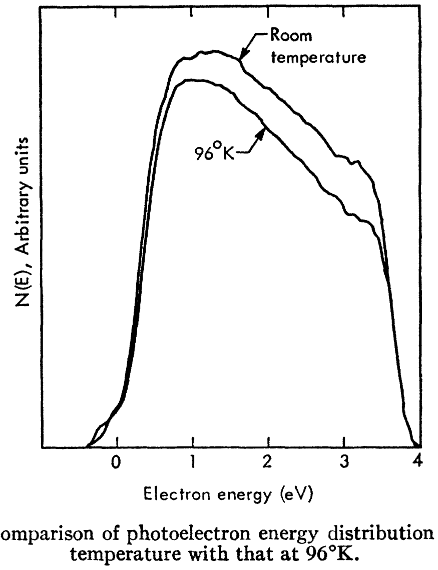

FIG. 7. Comparison of photoelectron energy distribution at room temperature with that at 96°K.

Figures 6 and 7 together demonstrate an increase in quantum yield in going from 96°K to room temperature, but no change between 45 and 96°K. The mechanisms of optical absorption and escape of photoelectrons are not understood well enough to permit an unambiguous explanation for the change in quantum yield with temperature. It might be related to a change in escape probability due to scattering of electrons by phonons. Another possibility is that it is simply related to a change in the optical absorption coefficient. If the fundamental optical absorption process is primarily an indirect (phonon-assisted) process, there is a greater probability of transitions involving phonon annihilation at higher temperatures.

The absorption coefficient for indirect transitions involving phonon annihilation is proportional to N_p, the phonon density, whereas for phonon creation it is proportional to (N_p+1). Phonons obey Bose-Einstein statistics, so that the photon absorption coefficients for transitions involving phonon annihilation and phonon creation are proportional to

$$[e^{h\omega_s/kT}-1]^{-1} \quad \text{and} \quad e^{h\omega_s/kT}[e^{h\omega_s/kT}-1]^{-1},$$

respectively. Substituting $k\Theta=h\omega_s$, where Θ is the Debye temperature and ω_s is the phonon frequency, a temperature dependence for the total absorption coefficient due to indirect transitions can be obtained. Using $\Theta=308°\text{K}$ for Zn,[9] the absorption coefficient has the relative values 1.27, 1.02, and 1.00 at temperatures 290, 96, and 45°K, respectively. The change in yield, as indicated by Figs. 6 and 7, is consistent with the estimated change in the absorption coefficient.

A change in optical absorption due to phonon-assisted transitions necessarily means a change in electron-phonon scattering after the initial excitation. Any change in escape probability due to electron-phonon scattering after excitation is energy dependent. The invariance of the shape of $N(E)$ with temperature lends credence to the suggestion that the change in yield is due largely to a change in the optical absorption coefficient. Perhaps of greater significance is that Monte Carlo calculations of photoemission show that the quantum yield is not sensitive to the electron-phonon mean free path for typical electron-electron scattering cross sections in metals.[10–12]

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