$\langle|\psi(0)|_{E_F}^2\rangle_{av} = 0.74$ gives a range for the ratio of 0.418 to 2.541, easily bracketing the measured value on the first zone.

A complete discussion of the method of analysis and the results of the entire field- and temperature-dependent study of σ in Cd are to be reported later.

The authors wish to thank Professor L. M. Falicov for several helpful discussions.

*Work supported by the U. S. Atomic Energy Commission. U. S. Atomic Energy Commission Report No. ORO-3087-35.

[1]M. L. Glasser, Phys. Rev. 150, 234 (1966).

[2]J. M. Reynolds, R. G. Goodrich, and S. A. Khan, Phys. Rev. Letters 16, 609 (1966).

[3]For a complete discussion of the FS of Cd see R. C. Jones, R. G. Goodrich, and L. M. Falicov, Phys. Rev. 174, 672 (1968).

[4]S. A. Khan, J. M. Reynolds, and R. G. Goodrich, Phys. Rev. 163, 579 (1967).

[5]L. M. Falicov and R. V. Kasowski, Phys. Rev. Letters 19, 795 (1967); and R. V. Kasowski, to be published.

[6]The use of $\tilde{\chi}_p/\chi_p = \tilde{n}/n$ has the advantage of scaling out the many-body interactions which cannot be calculated and may lead to as much as a 50% correction in χ_p and $\tilde{\chi}_p$. See Falicov and Kasowski, Ref. 5.

[7]We are indebted to T. R. McGuire and the staff of the IBM Thomas J. Watson Research Center for making these measurements.

[8]D. Shoenberg, in Proceedings of an International Conference on Electron Mean Free Paths in Metals, Zurich, Switzerland, 3-5 September 1968 (Springer-Verlag, Berlin, Germany, 1969), p. 1.

[9]C. G. Grenier, K. R. Efferson, and J. M. Reynolds, Phys. Rev. 143, 406 (1966).

PHOTOEMISSION OBSERVATION OF SURFACE-PLASMON EXCITATION IN THE ALKALI METALS*

Neville V. Smith
Bell Telephone Laboratories, Murray Hill, New Jersey 07974,†
and Stanford University, Stanford, California 94305

and

William E. Spicer
Stanford University, Stanford, California 94305

(Received 22 July 1969)

Measured energy distributions of photoemitted electrons from K, Rb, and Cs show a high-energy peak identified as unscattered (primary) electrons, and an intermediate peak at somewhat lower energies which is believed to be due to a plasmon energy loss. This intermediate structure becomes more pronounced and closer to the primary peak on proceeding from K to Rb to Cs. This systematic trend, together with the absence of any clearly discernible intermediate structure in Na, is consistent with the variation of the corresponding plasmon energies. In Rb and Cs the intermediate peak is sufficiently pronounced to permit its identification as a surface rather than a volume-plasmon excitation.

The electron-electron interaction has an important influence on the photoemission process.[1] The photoemission process is conventionally envisaged in three distinct steps: (1) optical excitation of electrons in the interior of the material, (2) transport of some of these electrons to the surface, and (3) escape across the surface. In the transport to the surface, the excited electrons are quite likely to suffer an inelastic scattering event before they can escape into the vacuum. Scattering by electron-electron interactions is believed to be the dominant process, and the scattering length is a rapidly decreasing function of energy.[2] The number of electrons which escape without scattering (primary electrons) is therefore severely diminished. Moreover, electrons which have undergone an inelastic scattering event may still be sufficiently energetic to surmount the potential barrier at the surface, and escape from the material as slower secondary electrons. It is these secondary photoelectrons which will concern us here.

An excited electron may decay through the electron-electron interaction by either of two basic mechanisms, pair creation or plasmon creation.[3] We include in the latter both surface- and volume-plasmon losses. The energy distribution of secondaries is expected to differ for these two mechanisms. The contribution to the energy distribution curve (EDC) due to secondaries pro-

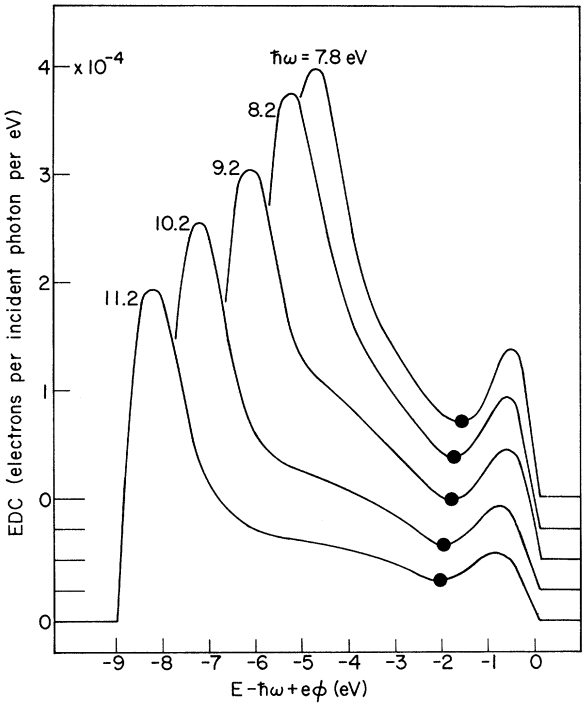

FIG. 1. Photoelectron energy distribution curves for K plotted against $E-\hbar\omega+e\varphi$.

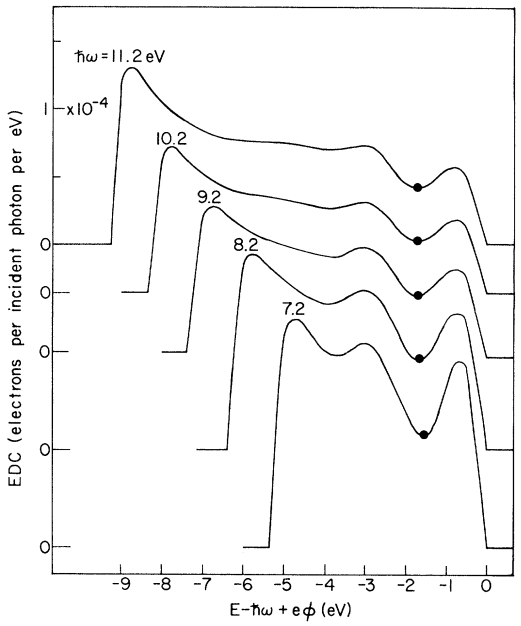

FIG. 2. Photoelectron energy distribution curves for Cs plotted against $E-\hbar\omega+e\varphi$.

duced by pair creation has been considered by Berglund and Spicer.[1] Due to threshold effects, one expects a peak very close to the low-energy cutoff. Above this the distribution decreases smoothly with increasing energy. Energy loss by plasmon creation, on the other hand, is discrete, and may be expected to give rise to its own characteristic structure in the EDC which is simply related to structure in the primary distribution. A peak in the energy distribution of primary electrons should have associated with it a secondary peak shifted down in energy by the plasmon energy. Evidence of such effects has been observed in photoemission from Ag, Pd, and Ni by Vehse, Stanford, and Arakawa,[4] and in cesiated Ni by Callcott and Macrae.[5] The alkali metals form an ideal system in which to look for these effects owing to the low values of their work functions, Fermi energies, and plasma frequencies. These features combine to bring the possibility of observing plasmon effects well within our accessible energy range.

Some experimentally measured EDC for potassium are shown in Fig. 1. These curves are plotted against $E-\hbar\omega+e\varphi$, where E is the electron kinetic energy in vacuum, $\hbar\omega$ is the photon energy, and $e\varphi$ is the work function. This choice of scale refers the photoelectrons to their initial energies, and places the zero of energy at the Fermi level. Each curve shows a peak at the high-energy end. We identify this leading peak as due to primary or unscattered photoelectrons. The free-electron Fermi energy is 2.1 eV so that all primary electrons must fall within this distance of the leading edge. The full circles represent the position of the valley and are taken as the low-energy demarcation of the leading peak. It can be seen that there is a tendency for the leading peak to get narrower with decreasing photon energy. The peak gets narrower at even lower photon energies. This effect may be understood in terms of the direct (i.e., $\vec{k}$-conserving) nature of the optical transitions and will be discussed at greater length elsewhere.[6] Our present concern is with the behavior of the EDC at energies below the leading peak. At the higher photon energies, the EDC show a sharp low-energy peak and a broad intermediate piece of structure in the −6- to −2-eV range. We identify this intermediate structure as a plasmon energy loss.

In Fig. 2 we show some corresponding curves for cesium. Again there is a leading peak which we identify as due to primary electrons (the free-electron Fermi energy is 1.5 eV), and an intermediate peak which we identify as a plasmon energy loss. The intermediate peak is more pronounced and closer to the primary peak, which is consistent with the lower plasma frequency in

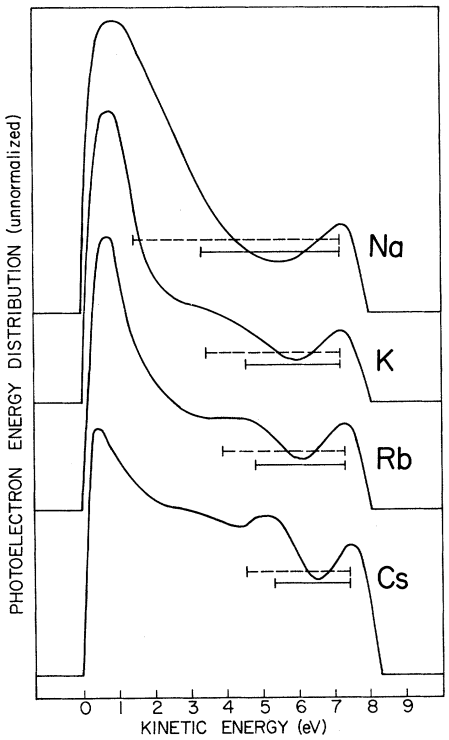

FIG. 3. Photoelectron energy distribution curves at $\hbar\omega = 10.2$ eV for Na, K, Rb, and Cs, plotted against E, the kinetic energy in vacuum.

cesium. The intermediate peak has also been seen in rubidium and is more pronounced than in potassium but less pronounced than in cesium. In sodium no intermediate peak can be clearly discerned.

Figure 3 shows the EDC at $\hbar\omega = 10.2$ eV for each of the four metals. The horizontal bars represent the magnitudes of the plasmon energies as determined by Kunz.[7] The full bars represent the surface-plasmon energies and the broken bars represent the volume-plasmon energies. It can be seen that the separations of the primary and intermediate peaks in cesium and rubidium agree quite well with the surface-plasmon energies; the volume-plasmon energy is definitely too large. In potassium the intermediate peak is too broad to permit any definite decision between surface and volume plasmons. The absence of any clearly discernable intermediate peak in Na is consistent with the larger plasmon energy for this metal. The low-energy peak in the Na EDC is noticeably wider than in the other metals. It is possible that there is an intermediate peak but that it is still buried in the low-energy peak. In fact, the 10.2-eV curve for Na bears some resemblance to the 7.8-eV curve for K, but on an expanded energy scale. We are presumably looking at Na at a much earlier stage in its evolution. This and the other systematic trends all appear to be in order. In Cs there is evidence of an additional piece of structure at energies just below the prominent intermediate peak. This is quite possibly a two-plasmon energy loss.

We conclude that the intermediate structure which we have observed in the EDC of alkali metals can be understood in terms of a plasmon energy loss. The structure is quite reproducible between different samples, which were thick evaporated films, and is independent of substrate material. The energy separation of the primary and secondary peaks, where it can be measured, leads us to prefer a surface- rather than a volume-plasmon mechanism.

The assistance of Galen Fisher in this work, as well as profitable discussions with John Endriz, is gratefully acknowledged.

---

*Part of this work was performed while one of the authors (NVS) was a research associate at Stanford University, and part while on assignment at Stanford University from Bell Telephone Laboratories. The facilities used at Stanford are supported in part by the Advanced Research Projects Agency through the Center for Materials Research at Stanford University and by the National Science Foundation.

†Permanent address.

[1]C. N. Berglund and W. E. Spicer, Phys. Rev. 136, A1030, A1044 (1964), and references given therein.

[2]Alternative models have been proposed. R. K. Nesbet and P. M. Grant, Phys. Rev. Letters 19, 222 (1967), suggest that electron-electron interactions should be included as part of the optical excitation event. L. Sutton and J. J. Hopfield (private communication) go further by suggesting that photoemission is more properly thought of as a one-step process in which the steps described above are closely interconnected. L. Hedin, B. I. Lundquist, and S. Lundquist, Solid State Commun. 5, 237 (1967), adopt a different approach by including plasmon and pair creation in the setting up of the electronic states prior to optical excitation. These various many-body approaches may indeed be more appropriate. From an experimental standpoint, however, the qualitative predictions of each model appear to resemble those of the three-step model. We therefore choose the three-step model as a conveniently simple framework in which to interpret our data without in any way ruling out these other possibilities.

[3]D. Pines, Elementary Excitations in Solids (W. A. Benjamin, Inc., New York, 1964), p. 151.

[4]R. C. Vehse, J. L. Stanford, and E. T. Arakawa,

Phys. Rev. Letters 19, 1041 (1967); R. C. Vehse and E. T. Arakawa, Phys. Rev. 180, 695 (1969).
[5]T. A. Callcott and A. U. Macrae, Phys. Rev. 178, 966 (1969).
[6]N. V. Smith and W. E. Spicer, to be published.
[7]C. Kunz, Z. Physik 196, 311 (1966).

DIELECTRIC CONSTANT AND MOBILITY OF A DOPED ZERO-GAP SEMICONDUCTOR

L. Liu*
Department of Physics, Northwestern University, Evanston, Illinois 60201,
and Gruppo Nazionale di Struttura della Materia, Sezione di Pisa, Italy

and

E. Tosatti
Scuola Normale Superiore, Pisa, Italy, and Gruppo Nazionale di Struttura della Materia, Sezione di Pisa, Italy
(Received 31 July 1969)

The concentration-dependent static dielectric constant is calculated for degenerate n-type α-Sn. The anomalous enhancement of the low-temperature and low-concentration electron mobility is explained.

The static dielectric constant $\epsilon(q)$ of α-Sn has been shown[1,2] to go to infinity like λ/q as $q \to 0$. This infinite dielectric constant in a semiconducting material is a consequence not only of the zero gap in the one-particle energy spectrum but also of the fact that the degeneracy of the band edge is symmetry induced. In any actual sample of α-Sn, however, the presence of impurity carriers is sufficient to remove this $1/q$ infinity. Instead, the intraband excitation contributes a term k_{FT}^2/q^2 to the dielectric constant, where k_{FT} is the Fermi-Thomas momentum. The interband part is now finite but is expected to have a strong dependence on the impurity concentration. This dependence is absent in a normal semiconductor.

In this paper we determine the concentration-dependent dielectric constant in a degenerate n-type sample of α-Sn. This calculated dielectric constant is used to evaluate the electron mobility at low temperature where impurity scattering is the dominant mechanism. The results are in excellent agreement with the experimental mobility values at 4.2°K.[3-5] Also included in the discussion are some general remarks about the dielectric constant in other zero-gap materials.

The calculation of the dielectric constant is based on the random phase approximation (RPA) expression[6] for $\epsilon(q)$ of a solid:

$$\epsilon(q) = 1 - \frac{4\pi e^2}{q^2} \sum_{r n' \vec{k}} \frac{|\langle \vec{k}, n | e^{-i\vec{q}\cdot\vec{r}} | \vec{k}+\vec{q}, n' \rangle|^2}{E_{\vec{k}+\vec{q}, n'} - E_{\vec{k}, n}} (N_{\vec{k}+\vec{q}, n'} - N_{\vec{k}, n}), \tag{1}$$

where the Bloch state $|\vec{k}n\rangle$ labeled by the reduced wave vector $\vec{k}$ and band index n has energy $E_{\vec{k}, n}$ and occupation number $N_{\vec{k}, n}$. The concentration-dependent interband polarizability $4\pi\alpha^{\text{inter}}$ for doped samples comes from the coupling between those filled valence and empty conduction states which are close to the band edge. This part we evaluate in detail. The contribution from all other states is taken to be a constant ϵ_0 whose value is known[7] to be 24.

To evaluate α^{inter}, we use the $\vec{k}\cdot\vec{p}$ value for the matrix element obtained by Liu and Brust[1]:

$$|M|^2 \equiv |\langle \vec{k}, c | e^{-i\vec{q}\cdot\vec{r}} | \vec{k}+\vec{q}, v \rangle|^2 = \frac{3}{4} \frac{q^2 \sin^2\theta}{k^2 + q^2 + 2kq\cos\theta}, \tag{2}$$

where θ is the angle between $\vec{k}$ and $\vec{q}$. For the energy differences, we assume spherical conduction and valence bands with effective mass values m_e^* and m_h^*, respectively, and neglect the ratio m_e^*/m_h^* compared with unity. For α-Sn, where $m_e^*/m_h^* \simeq 0.1$, this is a good approximation introducing