

Energy Distribution of Slow Positrons Diffusing from Incomplete *d*-Shell Transition Metals\*

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(Received 1 May 1974; revised manuscript received 13 August 1974)

The energy distribution of slow positrons diffusing from chemically cleaned and partial-outgassed polycrystalline tungsten, molybdenum, and chromium is made up of two principal parts, a broad asymmetric peak at  $0.2 \pm 0.1$  eV with a width of  $\sim 2$  eV, and a second sharp, usually symmetric, peak with an energy which depends upon the material under study. The second peak is believed to be associated with the bulk properties of the material, in particular, with the electronic density of states.

The energy distribution of slow positrons diffusing from a variety of materials has been studied in several laboratories.<sup>1,2</sup> In high-positron-yield materials like Cu and Au there is but one sharp peak at  $0.2 \pm 0.1$  eV with a full width at half-maximum (FWHM)  $\sim 0.35$  eV after correcting for the electron contact-potential difference (cpd) between the energy analyzer and the moderator<sup>3</sup> and the finite resolution of the analyzer. However, all metals do not produce such narrow distributions. In fact, none of those discussed in this note do.

In this report we discuss a new phenomenon which is observed for some of the incomplete *d*-shell transition metals. The energy distributions of the slow positrons from low-yield materials like W, Mo, and Cr show a second, nearly symmetric, narrow peak superimposed on the long decaying tail of the first. The position and intensity of the second peak depend on the material. Its width is less than 0.4 eV. This second peak is absent altogether in Ta, Zr, Nb, and Fe (data not shown), which belong to the same group of incomplete *d*-shell metals. While the present results are preliminary, they are of interest to those concerned with the positron behavior in metals. Hitherto, it was believed that in metals, positrons with energies around a few eV quickly thermalize, without being affected by the finer details of the electronic structure of metals. This does not appear to be the case for the metals under discussion here.

A brief description of the apparatus was given earlier.<sup>2</sup> The spectra of slow positrons were taken in a backscattering geometry shown in Fig. 1. All samples were at least 0.1 cm thick and the surfaces were mechanically polished to mirror finish using SiC paper and finally with a 4- $\mu$ m diamond polish. The samples were degreased, etched in HCl (1*N*), and finally rinsed

with distilled water before being introduced into the experimental chamber, maintained at a pressure below  $10^{-7}$  Torr. Because of the relatively high pressure we cannot expect ultraclean surface conditions. The time required to take each spectrum is several hours which would require a vacuum of at least  $10^{-11}$  Torr to insure less than a monolayer formation.

Fast positrons from a Co<sup>58</sup> radioactive source, electrodeposited on a copper grid, strike the polished surface of the moderator, and some of them reach equilibrium with the solid and diffuse back into the vacuum through the same surface. Those which leave the surface pass through the source grid to a Kuyatt-Simpson-type hemispherical electrostatic analyzer. The energy resolution was fixed at 0.12 eV (1.1%) by the acceptance angle  $\sim 5^\circ$ .

The cpd's for various samples, with respect to the electrostatic analyzer, are different and depend on the material and surface conditions of the samples. After the positron spectrum was taken an *in situ* experiment determined the onset of the

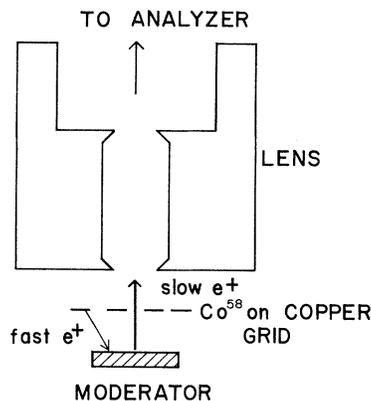


FIG. 1. Backscattering geometry.

spectrum of secondary electrons produced from the sample by the bombarding positrons and  $\gamma$  rays from the radioactive source. The difference between the zero of the energy scale (as measured by a meter) and the onset of secondary electrons (corrected for analyzer resolution) is the cpd. For these samples, where it is determined, the corrected zero of energy in vacuum is indicated by an arrow in Fig. 2.<sup>3,4</sup> For purposes of discussing the second narrow peak we

will refer all energies to the uncorrected energy scale, since this scale, in principle, relates to the zero of the kinetic energy of a positron inside the solid.<sup>5</sup>

The spectra of positrons from W, Mo, Cr, Ta, Zr, and Nb are shown in Fig. 2. Also the spectrum from an unbaked high-yield Cu sample is shown for comparison. Figure 2(a) is the spectrum for a polycrystalline W sample. The spectrum consists of a broad asymmetric peak at

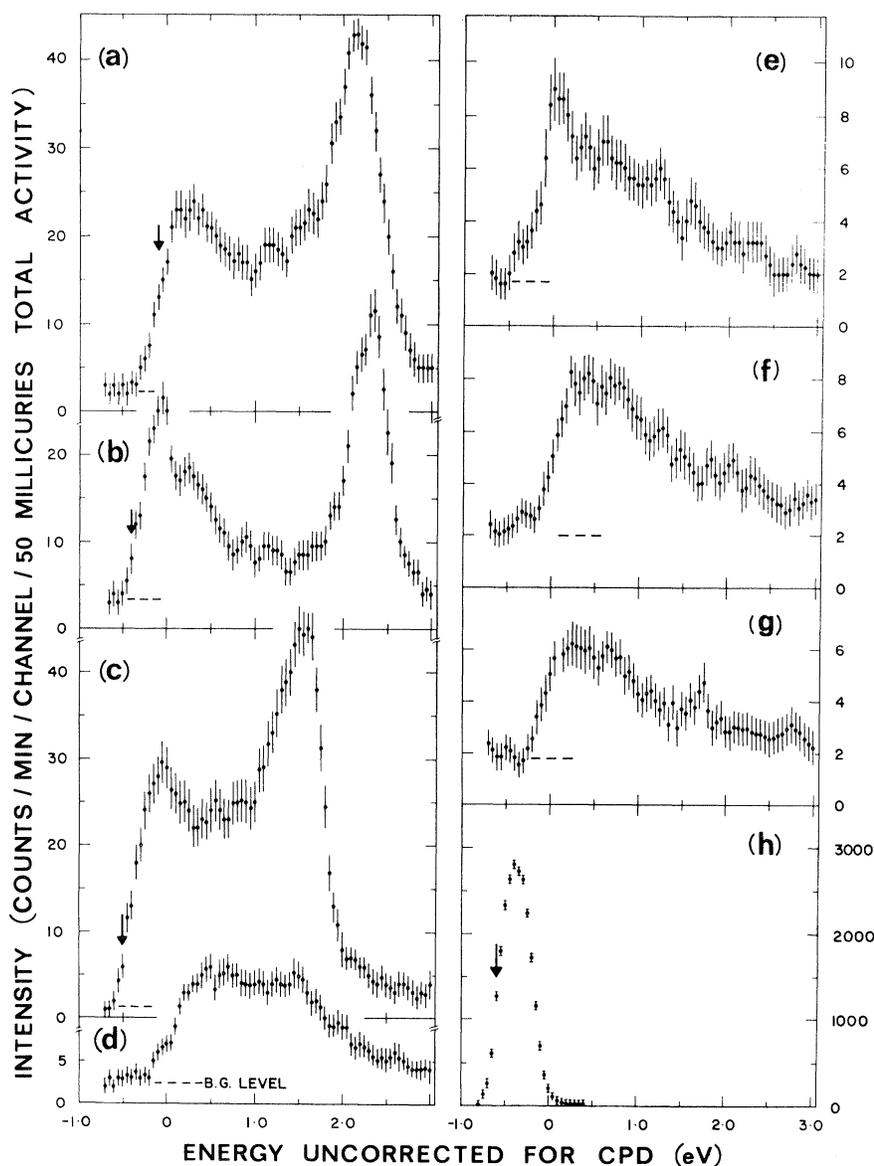


FIG. 2. Energy distribution of slow positrons diffusing from room-temperature polycrystalline (a) W, (c) Mo, (d) Cr, (e) Ta, (f) Zr, (g) Nb, and (h) Cu. In (b) the W sample was baked for 10 h at 475°K. Here the spectrum was taken at 475°K. The arrows and the horizontal dashed lines indicate the zero of the kinetic energy in vacuum after correcting for the contact potential difference and the background counting level in each case, respectively. Each channel is 50 meV.

$\sim 0.2 \pm 0.1$  eV with a width  $\approx 2.2$  eV. A relatively intense, sharp peak can be seen at  $2.2 \pm 0.1$  eV with a FWHM (corrected for resolution)  $< 0.4$  eV. The same sample was then heated to 475°K (the thermal limit of our heating element) inside the vacuum chamber for at least 10 h, and the spectrum was taken at 475°K [Fig. 2(b)]. After cooling the specimen to room temperature another spectrum was taken. The distribution was the same as the distribution in Fig. 2(b). Also spectra at room temperature were taken for a single-crystal W sample along the [110] and [116] directions. Except in the case of [116] direction, all of the spectra from different tungsten samples gave results similar to Figs. 2(a) and 2(b). The results from the [116] direction showed a substantial change in relative peak height and width for the second peak.

Figure 2(c) is the spectrum from an unbaked polycrystalline Mo sample which had been under vacuum for at least 8 h.<sup>6</sup> There are two distinct peaks as in the case of W, with the second peak around 1.6 eV.

The spectrum from an unbaked polycrystalline Cr sample is shown in Fig. 2(d). In this case the second peak in the vicinity of 1.4 eV is not clearly defined but is identifiable.

The results from Ta, Zr, and Nb are shown in Figs. 2(e), 2(f), and 2(g), respectively. These spectra have an asymmetric distribution similar to the first peak in W, but no second peak is observed.

It should be noted that there was nearly 0.4 eV change in the position of the first peak in 2(b) in comparison to that in 2(a), whereas the change in the position of the second peak was near 0.1 eV, the uncertainty of our measurements. We conclude that the large change in the position of the first peak upon heating is primarily due to change in cpd, and hence, the corresponding change in the barrier height (positron work function),<sup>5</sup> for the escaping positrons. The second peak is unaffected by surface conditions, thus reflecting bulk properties of the sample. By comparison, in the case of high-yield samples like Cu, shown in Fig. 2(h), a similar change in the specimen temperature produces a positive shift in the energy scale of approximately 0.6 eV and a corresponding decrease in intensity of more than 2 orders of magnitude.<sup>3,4</sup> In contrast to this, only a small change in yield is recorded in these experiments.

In virtually all cases studied in our laboratory any change in the magnitude of the low-energy

peak and a shift in the contact-potential difference can be related to a change in the surface conditions resulting from partial outgassing of the surface, which is also reflected in similar changes in the secondary-electron spectra from these samples.

Among the incomplete *d*-shell transition metals studied by us only W, Mo, and Cr, which belong to group VI<sup>B</sup> of the periodic table, produced double peaks. Ta and Nb, which belong to group VB, Zr, which belongs to group IV<sup>A</sup>, and Fe, which belongs to group VIII (results not shown here), produced a single asymmetric peak.

From the experimental results, the presence or the absence of a second peak in these metals can be correlated with the position of the electron Fermi level in the electron density-of-states curves for these metals.<sup>7</sup> When the Fermi energy is at a low-density point (only W, Mo, and Cr), that material gives rise to two peaks; whereas the second peak is absent (Ta, Zr, Nb, Fe) when the Fermi energy is at a high-density point in the density-of-states curve. Qualitatively the intensity of the first peak seems to be an inverse function of the electron density of states at the Fermi energy, for these two groups of metals. Our preliminary experiments clearly demonstrate that the energy distribution of slow positrons diffusing from metals, besides providing an understanding of the electrostatic barrier at the metal surface, apparently yield information about the electronic properties of the solid, analogous to the soft-x-ray spectroscopy of metals.

We would like to thank C. E. Kuyatt for his help in the design of the electrostatic analyzer and D. W. Lynch, J. D. Brown, and J. P. Marton for providing some of the samples and for their help in the preparation of the samples.

\*Work supported in part by the National Research Council of Canada and the Centre for Interdisciplinary Studies in Chemical Physics.

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<sup>1</sup>D. G. Costello, D. E. Groce, D. F. Herring, and J. Wm. McGowan, *Phys. Rev. B* **5**, 1433 (1972); W. C. Keever, B. Jaduszliwer, and D. A. L. Paul, in *Atomic Physics*, edited by S. J. Smith and G. K. Walters (Plenum, New York, 1972), pp. 561-571; P. G. Coleman, T. C. Griffith, and G. R. Heyland, *Proc. Roy.*

Soc., Ser. A 331, 561 (1973).

<sup>2</sup>S. Pendyala, P. W. Zitzewitz, J. Wm. McGowan, and P. H. R. Orth, Phys. Lett. 43A, 298 (1973).

<sup>3</sup>S. Pendyala, D. Bartell, F. E. Girouard, and J. Wm. McGowan, to be published.

<sup>4</sup>F. E. Girouard, S. Pendyala, D. Bartell, and J. Wm. McGowan, in Proceedings of the Thirty-Fourth Physical Electronics Conference, Bell Telephone Laboratories, Murray Hill, New Jersey, 1974 (unpublished).

<sup>5</sup>B. Y. Tong, Phys. Rev. B 5, 1436 (1971); C. H. Hodges and M. J. Stott, Phys. Rev. B 7, 73 (1973).

<sup>6</sup>In Ref. 1, Keever, Jaduszliwer, and Paul reported changes in positron intensities for high-yield material

like Ni in periods of a few hours after introducing the sample into the vacuum system. Similar behavior for Cu, Ni, Au was observed in our laboratory (Ref. 3) over a period of several days, perhaps because of pumping on the sample at  $10^{-7}$  Torr. However, no significant changes in yield have been observed for any of the low-yield samples reported here over a period of one week in some cases, even though peak shifts associated with baking were very noticeable.

<sup>7</sup>See, for example, *Electronic Density of States*, U. S. National Bureau of Standards Special Publication No. 323, edited by L. H. Bennett (U. S. GPO, Washington, D. C., 1971), pp. 31, 54, 55, 222.

## Absolute Conduction- and Valence-Band Positions for Ge from an Anisotropic Model of Photoemission\*

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(Received 5 August 1974)

An anisotropic direct-transition model for single-crystal semiconductors is shown to predict the direct-transition features seen in experimental photoemission spectra for Ge(111) for  $h\nu \lesssim 20$  eV. By comparing theory with experiment, all the conduction and valence bands at  $L$  and  $X$  within 1 Ry of the gap are determined. Comparison of experiment with current band models suggests that an  $\sim 10\%$  self-energy correction may be needed to describe high-energy optical transitions.

Germanium is a prototype semiconductor for band-structure studies, and a variety of experimental techniques have been applied to the determination of selected aspects of its band structure. These have included optical measurements<sup>1,2</sup> (which determine energy-band separations), photoemission measurements interpreted using symmetry line analyses,<sup>3,4</sup> and photoemission valence-band overviews<sup>5</sup> (which give overall bandwidths).

In spite of the large amount of information represented by the above studies, many significant features of the valence and conduction bands of Ge have remained undetermined. In the present paper, we obtain from photoemission and optical data all the energy-band eigenvalues for Ge at  $L$  and at  $X$  within  $\sim 1$  Ry of the gap using an analysis which contains two fundamental new results. There is, first, a demonstration that the anisotropy in photoexcited electron transport to and escape through a  $\langle 111 \rangle$  cleaved surface is vital for obtaining calculated spectra which replicate experimental spectra for  $h\nu \approx 15$  eV. Second, experimental band positions are determined by com-

paring data with features in theoretical spectra which include those which arise from transitions at *general points*<sup>6</sup> in the Brillouin zone (BZ).

Besides our determination of Ge band positions over a wide range of conduction- and valence-band energies, there are three other implications of this work. These are the demonstration that final-state crystal-momentum information is preserved in the transport and escape steps of the photoemission process for cleaved semiconductor surfaces; the observation that direct-transition features are seen in spectra for all  $h\nu \approx 20$ –25 eV; and the realization that a "self-energy" term, e.g., one linear in energy, appears to be needed in the Hamiltonian to produce the proper high-lying conduction-band structure.

Our anisotropic model starts with the energy bands  $E_n(\vec{k})$  determined by the  $l=2$  nonlocal pseudopotential described by Phillips and Pandey.<sup>7</sup> This potential has been shown<sup>7</sup> to provide a good description of valence bandwidths and low-lying optical transitions in Ge. Photoemission spectra  $P(E_i, h\nu)$  for primary (unscattered) electrons, from states of initial energy  $E_i$ , are then calculated using an anisotropic, direct-transition model<sup>8</sup>:

$$P(E_i, h\nu) = K \sum_{n,n'} \int d^3k \{ \delta(E_n(\vec{k}) - E_i) \delta(E_{n'}(\vec{k}) - E_i - h\nu) | \vec{P}_{mn'}(\vec{k}) |^2 D_{n'}(\vec{k}) T_{n'}(\vec{k}) \}. \quad (1)$$