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Observation and Interpretation of the Auger Electron Spectrum from Clean Beryllium*

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Auger electron peaks at 92 and 104 eV have been observed in the derivative $dN(E)/dE$ of the secondary-electron energy distribution $N(E)$ from clean polycrystalline beryllium. Existence of these two Auger transitions can be explained in terms of conduction-band electrons with s character and p character and is consistent with theoretical calculations. The observed Auger transitions can be expressed as $1s2s2s$ (92 eV) and $1s2p2p$ (104 eV).

The band structure of beryllium has been the subject of recent theoretical investigations.¹⁻³ However, the only reported experimental evidence of the band structure has been x-ray-emission results. Agreement between recent K -emission results^{4,5} and the theoretical calculations is good near the Fermi level, but the theoretical results predict a much higher electron density near the bottom of the valence band. Since the x-ray-emission results are limited to transitions between the K shell (s symmetry) and the valence electrons having p symmetry,⁶ the K -emission results do not provide information on the valence electrons having s symmetry. In this Letter the beryllium Auger-electron spectrum is presented and is shown to be consistent with the cited theoretical calculations and K -emission results. In particular, the observed Auger electron transitions involve both $2s$ - and $2p$ -band electrons, and information is obtained on the total density of occupied states $n_T(\epsilon)$.

The experimental arrangement was essentially that described by Palmberg.⁷ An electron beam was incident at 60° from the target normal and 90° from the axis of the retarding-field spectrometer. A 2-keV beam was employed to determine contamination levels, and a 750-eV beam produced the beryllium Auger spectra. The retarding grids were modulated with a 200-Hz, 2-V (rms) sinusoidal signal. The beryllium was held between tantalum supports which permitted Ohmic

heating of the specimen.

Since the ~ 100 -eV beryllium Auger electrons can only escape from the near-surface region without appreciable energy loss, surface contamination of the beryllium must be small if the Auger spectrum of clean beryllium is to be observed. A clean beryllium surface was obtained by heating a high-purity beryllium specimen at an optical pyrometer temperature of $\sim 1350^\circ\text{K}$ in a vacuum of $\sim 10^{-8}$ Torr until the Auger peaks from all impurities were below the limits of detection. Oxygen impurity was the most difficult to eliminate; but for clean surfaces the ratio of the peak-to-peak amplitude of the oxygen Auger peak to the sum amplitude of the beryllium peaks was < 0.002 . From measurements on fully oxidized beryllium, this ratio was estimated to correspond to < 0.03 monolayer of oxygen. Beryllium from the bulk is believed to diffuse to the surface providing a clean beryllium surface. This belief was fostered by results with a quadrupole mass spectrometer in line with the heated beryllium: During the cleaning procedure a mass-9 (Be) peak was observed to be up to fifty times the noise level, whereas no peak was detectable at mass 25 (BeO) and no increase was seen in either mass 16 (O) or 32 (O₂).

The result for the clean beryllium Auger spectrum in the form of the derivative $dN(E)/dE$ of the secondary-electron energy distribution $N(E)$ is given in Fig. 1. In agreement with convention,



FIG. 1. Auger electron spectrum for clean polycrystalline beryllium.

the peak energies are listed at the maximum negative deflection. The Auger peaks at 92 and 104 eV have essentially the same peak-to-peak amplitudes. The possibility that the Auger peak at 92 eV was due to the presence of silicon was eliminated by auxiliary ionization loss measurements which revealed only the beryllium loss. Such ionization loss measurements clarify ambiguous cases in Auger electron spectroscopy.⁸⁻¹⁰

This Auger result can be related to the density of states $n(\epsilon)$ in the manner employed by Hagstrum,¹¹ Amelio and Schiebner,¹² and Amelio.¹³ Although these references neglect the dynamical effects of the coupling between the deep hole and the electron-hole interactions,¹⁴ their approach is sufficient for the present discussion. The Auger distribution is

$$f(\epsilon) = \int g(\epsilon + \Delta)g(\epsilon - \Delta)d\Delta, \quad (1)$$

where Δ is one-half the initial-state separation of the two band electrons participating in the Auger transition and $g(\epsilon)$ is the transition density, essentially a product of the Auger transition-matrix elements and the density of states $n(\epsilon)$. The integration is over all Δ such that the initial and final states are within the band. Thus if the transition-matrix elements have a weak energy dependence, peaks in $n(\epsilon)$ will be mirrored as peaks in $f(\epsilon)$. Furthermore, if the total density of states $n_T(\epsilon)$ is considered to be the sum of the density of states for band electrons with s char-

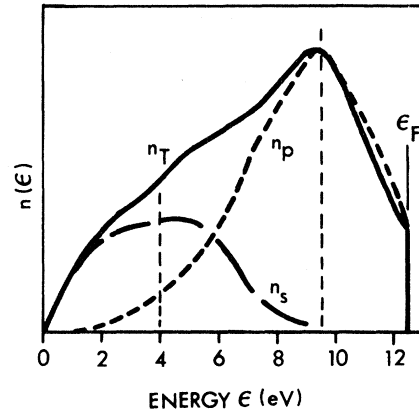


FIG. 2. Electron density of states for clean beryllium: $n_T(\epsilon)$ is the calculated total density of states (see Ref. 3); $n_p(\epsilon)$ is the partial density of states for electrons with p symmetry as determined from x -ray emission experiments (see Ref. 4); and $n_s(\epsilon)$ is the partial density of states for electrons with s symmetry and is given by the difference between $n_T(\epsilon)$ and $n_p(\epsilon)$.

acter and with p character,¹⁵

$$n_T(\epsilon) = n_s(\epsilon) + n_p(\epsilon), \quad (2)$$

then, formally,

$$f(\epsilon) = f_{ss}(\epsilon) + f_{sp}(\epsilon) + f_{pp}(\epsilon), \quad (3)$$

where $f_{ij}(\epsilon)$ is the Auger distribution with the i - and j -character band electrons participating in the transition.

The distribution of s -character and p -character electrons in the conduction band of beryllium is indicated in Fig. 2. Here $n_s(\epsilon)$ was determined by subtracting the experimental⁴ K -emission density of states $n_p(\epsilon)$ from the theoretical³ total density of states $n_T(\epsilon)$; $n_T(\epsilon)$ and $n_p(\epsilon)$ were normalized to represent the same density at the Fermi energy ϵ_F . A similar result was calculated by Altmann and Bradley.² These results are consistent with the band calculations of Loucks and Cutler,³ which show only s -character electrons at the bottom of the band. Figure 2 suggests that for a beryllium K -shell binding energy of 11 eV,¹⁶ a work function of 5.1 eV,¹⁷ and a Fermi energy of 12.2 eV,³ $f(\epsilon)$ Auger peaks should be observed at 89.5 eV ($1s2s2s$), 95.0 eV ($1s2s2p$ and $1s2p2s$), and 100.5 eV ($1s2p2p$). These values do not include a correction for the contact-potential difference between the sample and the analyzing grids.

Since data in Fig. 1 represent $df(\epsilon)/d\epsilon$, zeros in the Auger data correspond approximately to peaks in $f(\epsilon)$. The pertinent zeros occur at 88 and 99 eV, and the correlation with calculated

$1s2s2s$ and $1s2p2p$ transitions is good. However, the important correspondence is the energy difference of 11 eV between peaks in both the calculated and the observed cases; this energy difference is independent of the values taken for the binding energy, contact-potential difference, and the Fermi energy. Absence of the $1s2s2p$ and $1s2p2s$ peak may be due to the nature of its distribution, a small transition probability, poor resolution capability of the analyzing conditions, or any combination of the above. The relative amplitudes of the $1s2s2s$ and $1s2p2p$ peaks may be explainable in terms of two different transition probabilities.

Our results indicate that Auger transitions can be very sensitive to electronic band structure and can be valuable for determining band information when x-ray techniques are not completely suitable; however, $N(E)$ data corresponding to $f(\epsilon)$ Auger peaks would be more informative than $dN(E)/dE$ data. A background-nulling technique¹⁸ should be useful in obtaining worthwhile $N(E)$ data.

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Photoelectric Emission of RbCl in the Extreme Ultraviolet

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The spectral photoelectric yield of RbCl has been determined in the photon energy range 10 to 40 eV by using synchrotron radiation as a continuous light source. Comparison of the absorption spectrum with the spectral yield measured with and without retarding potential reveals that the general features of the spectral yield are attributable to electron-electron scattering and the absorption spectrum. The yield exceeds unity in the region 21.0 to 25.0 eV, and the electron affinity is estimated to be 0.50 ± 0.05 eV.

The quantum yield of RbCl was measured by Metzger¹ up to 21 eV. According to his results, the electron affinity χ was estimated to be 0.40 eV, assuming that the minimum of the spectral yield at 17.2 eV should be observed at $2(E_g + \chi)$, where E_g is the band-gap energy. The photo-

electric emission did not closely correspond with the absorption spectra. He concluded that the magnitude of the quantum efficiencies at photon energies greater than the minimum at $2E_g$ implies multiple processes to be dominant. Recent experiments on the photoemission of alkali ha-