Detection of gaps in the energy spectrum of lithium

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Two clearly defined maxima have been observed in the electron-photon emission spectrum of lithium, measured for the first time. These maxima are linked with particular features of the dispersion law for electrons in unfilled bands. It is shown that band-theory calculations can be tested by direct experiments.

Direct measurements of the Fourier components of a pseudopotential are clearly of interest for testing band-theory calculations and for testing the descriptions of the galvanomagnetic and optical properties of metals. Even for simple metals such as lithium, the value of V_{110} in the bcc phase is not known, since the optical properties of lithium have anomalous features that have yet to be explained,[1] and as the temperature is lowered (as it must be for observation of the De Haas-van Alphen effect), lithium undergoes a martensitic transition. We have accordingly carried out a theoretical and experimental study of the electron-photon emission spectra of lithium with the goal of detecting gaps in the lithium electron spectrum. The electron-photon emission—the emission of light during the bombardment of a metal by low-energy electrons[2–4]—contains unique information on the energy structure of unfilled electronic states. This method is presently being developed rapidly, and new opportunities are continually arising.

Lithium films about 1000 Å thick were deposited on sapphire substrates at room temperature. The films had a matte finish at an evaporation rate of 10–20 Å/min and at a residual gas pressure $\mathscr{P} \simeq 5 \times 10^{-6}$ Pa. The pressure during the measurements was $\mathscr{P} \leqslant 2 \times 10^{-7}$ Pa. An electron beam with a current density up to 70 A/m^2 and

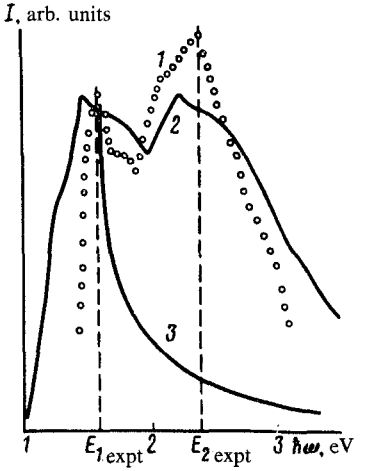

FIG. 1. Electron-photon emission spectra of lithium. 1—Experimental; 2—exact calculation; 3—two-wave approximation.

with an electron energy of 200–300 eV struck the target surface at an angle of 45°; the emission was monitored at an angle of 15°. The spectra were recorded under photon counting conditions by the apparatus described in Refs. 2 and 4. About 1 h was required to record a spectrum.

The points in Fig. 1 show the number of photons, N, versus their energy E. This spectrum could be reproduced repeatedly when lithium was redeposited on the surface of the sample after the electron bombardment or after the sample was left in the residual gas atmosphere for several days. The reproducibility of these experimental results indicates that no significant changes of importance to the electron-photon emission spectrum occur in the properties of lithium. This reproducibility may also be taken as evidence that the emission observed is of a volume nature. It can be seen from curve 1 in Fig. 1 that there are two clearly defined maxima in the electron-photon emission spectrum, along with several other reliably observed structural features.

We carried out a pseudopotential calculation of the band energies and wave functions in an effort to interpret these structural features. In the calculations we used Heine-Abarenkov pseudopotential form factors, localized on the Fermi sphere and derived from "first principles"[6]: $V_{110}=0.10367u$, $V_{200}=0.06901u$, and $V_{211}=0.01768u$, where $u=(\hbar^2/2m)(2\pi/a)^2$, $a=6.618$, and a_B is the lattice constant of lithium. The spectrum of the electron-photon emission due to direct interband transitions is[2]

$$N(E) \sim \frac{2\pi}{\hbar} \sum_{i,f,k} |\langle ik|\hat{H}_{\text{rad}}|fk\rangle|^2 \delta(\epsilon_{ik}-\epsilon_{fk}-E)\Phi(\epsilon_{ik})[1-f_F(\epsilon_{fk})]\rho(E), \tag{1}$$

where $\rho(E)$ is the state density of the photon field, the operator $\hat{H}_{\text{rad}}$ represents the interaction with the light, $\Phi(\epsilon_{ik})$ is the energy distribution of nonequilibrium electrons,

TABLE I.

Gap	Expt.	Teo.	Ref. 7	Ref. 8	Ref. 9	Ref. 10
$E_1 = E(N_1) - E(N'_1)$, eV	1.6	1.5	1.5	2.9	2.8	2.9
$E_2 = E(F_1) - E(F_3)$, eV	2.4	2.3	2.0	–	3.4	0.5

and $f_F(\epsilon)$ is the Fermi-Dirac function. As in Refs. 2–5, we assumed that the constant distribution function $\Phi(\epsilon_{ik})$ is nonvanishing for only the few lowest-lying bands: $i = 1$, 2, 3, 4.

Curve 2 in Fig. 1 shows the electron-photon emission spectrum calculated in this manner, within a constant factor. The peak in the spectrum at $E_{1\text{teo}} = 1.46$ eV, which corresponds to transitions near the point N, $(2\pi/a)$ (1/2, 1/2, 0) of the Brillouin zone, was predicted by Geguzin.[5] Curve 3 in Fig. 1 shows the spectrum according to the two-wave approximation[5] with $E_{1\text{expt}} = 1.6$ eV. Because of the higher-lying bands, the calculated value of $E_{1\text{teo}}$ differs substantially from the prediction of the two-wave approximation, $2|V_{110}| = 2.54$ eV. The peak near 2.4 eV corresponds to transitions between nearly parallel bands along the F direction in the Brillouin zone near the point $(2\pi/a)$ (2/3, 1/3, 1/3). In the empty-lattice approximation, the first three bands are degenerate at this point. The crystal potential based on these three bands alone leads to a splitting of the third band by an amount $3|V_{110}| = 3.81$ eV. This gap also decreases substantially, to $E_{2\text{teo}} = 2.28$ eV, according to our exact calculations. The ratio $E_2/E_1 = 3/2$ that follows from the approximate calculation agrees well with the result of the exact calculation and—a particularly important point—with the experimental data. This agreement means that calculations for various effects from the equations of the two-wave approximation can use an effective pseudopotential form factor, $|V_{110}^{\text{eff}}| = 0.8$ eV according to our measurements. The introduction of an effective pseudopotential of this type has been justified theoretically by inverting the secular equation by means of Löwdin's perturbation theory.

It can be seen from Fig. 1 that both the shape of the calculated spectrum and the positions of the peaks in it agree well with the experimental data. This agreement means that the model used here correctly reflects the basic aspects of electron-photon emission, so that the measured spectra can be used to test band calculations. Several band calculations have been carried out for lithium over the past few decades by various investigators, using various methods. In the present study it has been possible for the first time to compare the results of some of these calculations with direct experimental data. Table I demonstrates the important discrepancy between the results reported by different investigators. The results that agree best with our measurements and our own calculations are the results derived by Schneider and Stoll.[7] We should emphasize that our calculations have been based on pseudopotential form factors that contain no adjustable parameters. If desired, one could adjust the parameters to fit the positions of the structural features exactly to the experimental positions, as is done in the semiempirical pseudopotential method for semiconductors.

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