Inverse photoemission and electron–photon spectroscopy of lithium

Yu. M. Kobzar', V. G. Kovtun, N. I. Pashechko, and V. M. Shatalov
G. V. Karpenko Physicomechanical Institute, Academy of Sciences of the Ukraine

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The photon emission spectrum of lithium during bombardment with electrons with energies of 5–200 eV has been studied. Four structural features found in the photon energy interval $\hbar\omega = 1.65$–3 eV are linked with energy gaps in the electron dispersion and with Rydberg surface states. A restructuring was observed in the electron spectrum in the course of low-temperature martensitic *bcc–hcp* transition.

A number of recent papers have reported research on the structure and properties of alkali metals.[1,2] How important are exchange-correlation effects in the observed properties of these metals? We are referring here to the depth of the potential well, the width of the plasmon peak, the interband absorption edge, charge density waves, surface states, the low-temperature martensitic *bcc–9R–hcp* structural transition, etc. Recent results obtained on single crystals of alkali metals by high-resolution apparatus show that it is a complex task to explain these experiments.[1,2]

In this letter we are reporting the results of an experimental study of lithium by electron–photon spectroscopy,[3] specifically, by the inverse-photoemission method. A fundamentally distinctive feature of this method is that an outer electron with a low energy on the order of E_F, goes into a vacant energy level above the Fermi level E_F and then undergoes a radiative transition to a lower-lying state. Since the energy of the primary electron is low, no additional perturbations are caused by the electron scattering.

The experiments were carried out in ultrahigh vacuum on a USU-4 apparatus. Lithium films were heat-deposited on a Si(111) substrate. The parameters of the probe electron beam were varied over the ranges $E_p = 5$–200 eV and $I = 0.5$–1 mA/cm^2. The emission was detected by an FÉU-79 photomultiplier operating in the photon counting mode. The dispersive element was an MUM-2 grating monochromator.

In the lithium emission spectrum (Fig. 1) we find four structural features at photon energies between 1.68 and 3.1 eV. We link the positions of three of these features with the positions of three energy gaps above the Fermi level: one along edge *PH* and two others in the (110) and (100) directions, at the *N* and *H* points on the boundary of the Brillouin zone (Fig. 2). The literature reveals a fairly large number of calculations on the band structure of lithium, but all these calculations have led to different values of the energy gaps. Unfortunately, there are also ambiguities in the experimental data.[4]

Line *c* in Fig. 1 shows a spectrum calculated with allowance for inelastic scattering of nonequilibrium electrons.[5] This curve has two characteristic features, at $E_1 = 1.50$ eV and $E_2 = 2.75$ eV, which correspond to energy gaps on the boundary of

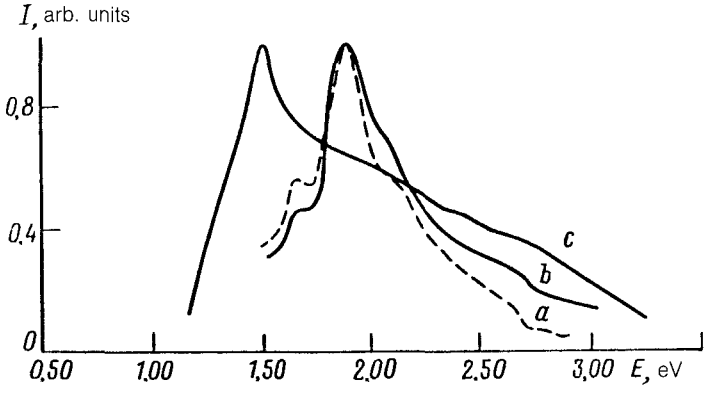

FIG. 1. Electron–photon emission spectra of lithium at two energies of the bombarding electrons. *a*—15 eV; *b*—100 eV. Line *c* is a calculated spectrum.

the Brillouin zone, along the *PNH* and *PH* edges, respectively. With increasing distance from the energy gaps to the Fermi level, the intensity falls off, so the structural feature at the *N* point is the most prominent. If level broadening is ignored, the position of a structural feature is equal to twice the value of the crystal potential in the given direction in the crystal. Working from the spectrum in Fig. 1 (lines *a* and *b*), we can therefore find the values of the pseudopotential at the *N* and *H* points: $V_{110} = 0.90$ eV and $V_{100} = 1.05$ eV, respectively. The size of the gap along the *PH* edge is 2.65 eV (Ref. 5).

As the energy of the bombarding electrons is raised, there are significant increases in the height and width of the structural feature associated with the transition from the N_1 state to the N_1' state at the *N* point, since this is the point closest to the Fermi level (line *b* in Fig. 1).

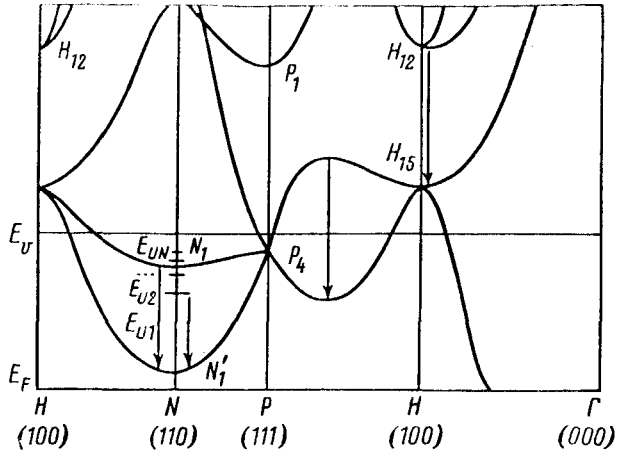

FIG. 2. Diagram of the lithium band structure. The arrows show observed transitions.

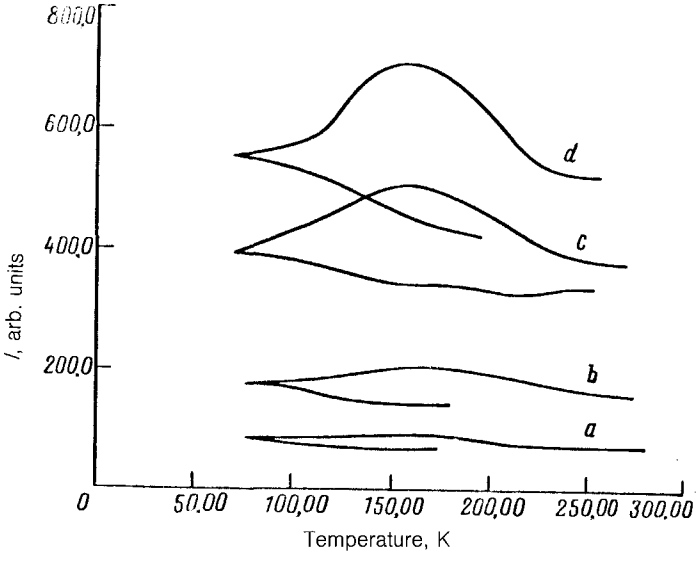

FIG. 3. Temperature dependence of the intensity of the emission from lithium for a primary-electron energy of 145 eV. a—The energy of the photons detected is 2.98 eV; b—2.70 eV; c—2.30 eV; d—1.90 eV. The upper branches of the curves correspond to cooling, and the lower ones to heating.

Near a photon energy $\hbar\omega = 1.72$ eV we find a structural feature (Fig. 1) which we do not link with the bulk energy structure. It is more likely associated with an emission which occurs upon a transition of nonequilibrium electrons from the E_{U1} state (Fig. 2), which lies 0.85 eV below the vacuum level E_V, in a gap formed by the projection of the bulk band structure onto the (110) surface. This emission stems from the effect of the image potential on the N_1' state near the N point. The states E_{U1}, E_{U2}, ..., E_{UN} are called "Rydberg surface states."[6]

When the lithium is cooled, the photon emission intensifies down to the temperature $T = 155$ K, and then weakens (Fig. 3). When the temperature is changed in the opposite direction, i.e., when the sample is heated, the curve is nearly the same in nature, but the intensities are significantly lower. Different parts of the spectrum react in different ways to a cooling of the sample; i.e., the martensitic transition involves the structural feature in the (110) direction. This feature is associated with transitions of nonequilibrium electrons near the N point (the N_1–N_1' gap; $\hbar\omega = 1.81$ eV). The increase in the emission intensity down to $T = 155$ K is due to a significant change in the phonon spectrum in the (110) direction, specifically, a softening of the TA phonons near the boundary of the Brillouin zone.[1] This effect leads to an increase in direct radiative transitions at the N point. We do not rule out the possibility that it is specifically the proximity of the N_1–N_1' energy gap to the Fermi level which is the most important factor in determining the directionality of the martensitic transition. Many-particle interactions give rise to a $9R$ structure.[7] When the temperature $T = 155$ K is reached, the buildup of defects results in a significant optical anisotropy and a decrease

in the photon emission. During the return heating cycle, we observe a hysteresis in the intensity, as is characteristic of properties of a substance during a martensitic transition.[1] The intensity decreases to $T = 165$ K and then begins to increase slightly, but the structural defects prevent it from reaching its former level.

In summary, it can be concluded that both in the case of the bulk band structure, during the formation of the $9R$ structure, and in the case of surface resonances, we need to go beyond the approximation of nearly free electrons in order to explain the observed features. It becomes necessary to invoke a theory which includes the effect of the exchange-correlation potential both in the volume and at the surface.

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