Observation of energy superstructure in lithium

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(Submitted 29 August 1989)
Pis'ma Zh. Eksp. Teor. Fiz. **50**, No. 7, 323–324 (10 October 1989)

The electron-photon emission of lithium at photon energies 0.23–3 eV have been studied. Several structural features have been detected for the first time in the emission spectrum of lithium. On the basis of these features it was assumed that charge-density waves produce an energy superstructure.

The systematic features and the new limit of the absorption edge in the far-infrared region of ordinary metals with nearly free electrons have recently been studied extensively, both theoretically[1,2] and experimentally.[3–5] In the present letter we report the results of an experimental study of anomalous behavior of the spectrum which consists not in absorption but in the inverse effect: electron-photon emission—nonequilibrium electrons emit radiation upon transition from excited energy states to lower states because of the intraband and interband transitions due to bombardment of the metal with slow electrons. The target, a thick lithium film, was synthesized by vapor disposition of a batch of 99.99%-pure Li from a quartz crucible in a vacuum of 7×10^{-8} Pa. The lithium was deposited on a substrate of silicon single crystal Si (111). The experiments were carried out using an ultrahigh-vacuum device with a sapphire window for the escape of light. Light in the visible region was recorded by a FEU-84 photomultiplier under photon counting conditions and in the infrared region it was recorded by a cooled photo-resistor under synchronous detection conditions.

In the visible region (Fig. 1) we observed two striking peculiarities at $E_1 = 2.85$ eV and $E_2 = 1.85$ eV. The position of these features is in good agreement with the calculations[6,7] which show that E_1 and E_2 are attributable to the direct interband transitions near the points N and F of the energy band structure of lithium. This circumstance made it possible to determine the Fourier components of the pseudopotential, $V_{110} = 1.43$ and $V_{200} = 0.93$ eV.

Of greatest interest turned out to be the detection of the singularity at $E_3 = 0.23$

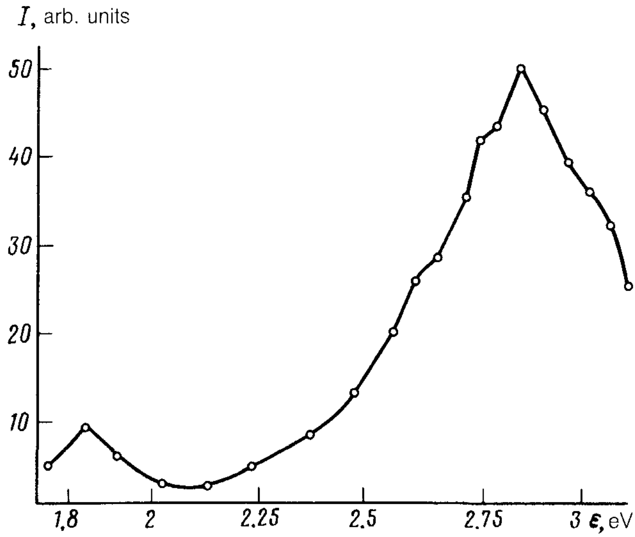

FIG. 1. The electron-photon emission spectrum of lithium in the visible region.

eV (Fig. 2), which was not predicted in studies of the electronic structure of lithium. The exception is the study of Overhauser,[8] in which he suggested that lithium has charge-density waves and that accordingly these waves produce a superstructure with various energy gaps between the bands built from the wave vector of the charge-density waves. The singularities of the spectrum of recombination radiation of electrons, which are driven to these bands by an external source, are the consequence of dispersion of the unoccupied states. As suggested in Ref. 9, the radiation spectrum

FIG. 2. The electron-photon emission spectrum of lithium in the IR region [O—295 K; △—77 K; ×—4.2 K).

contains singularities at photon energy equal to twice the value of the energy gap at the band boundary.

The results of a study using lithium film deposited on a substrate cooled to 77 K did not alter the results of the experiment. A lowering of the lithium temperature from room temperature to liquid-nitrogen temperature, on the other hand, affected appreciably the shape of the spectrum (curves 1 and 2 in Fig. 2). A change in the slope of curve 2 at the base of the singularity E_3 upon cooling is probably due to a decrease in the contribution of radiative intraband transitions. A significant increase in the intensity of the singularity E_3 upon lowering the lithium temperature to 4.2 K (curve 3 in Fig. 2) is caused by martensite transformation in the lattice and hence by a greater stabilization of the charge–density waves of the structure, which in turn increases the number of transitions with $\hbar\omega = 2\alpha$ where 2α is the energy gap between the bands created by the charge-density-wave potential.

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Translated by S. J. Amoretty