Electronic structure and optical spectra of heavy alkali metals at high pressures

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The first microscopic calculations of the optical characteristics of Rb and Cs at high pressures are reported. The changes in the reflection coefficient $R(\omega)$ observed experimentally are shown to result from an increase in the hybridization of s- and d-bands which occurs during hydrostatic compression.

The alkali metals are favorite materials for research in high-pressure physics. They have attracted interest because of their many phase transitions at moderate pressures. A prominent phase transition is the isostructural fcc–fcc transition in Cs, which occurs with a decrease in the specific volume at[1] 42 kbar. In accordance with Fermi's idea, it has been suggested that the electronic structure of Cs undergoes a pronounced change at this pressure: the $6s$-band empties, and the $5d$-band becomes filled. Since the $5d$-electrons are localized to a greater extent, the result is a decrease in the specific volume of the crystal.[2] This idea has led to the suggestion of similar transitions in[3,4] Rb and K, but they have not been observed experimentally.

With the advent of self-consistent calculations of the electronic structure, it became clear that the picture of the s-d transition drawn above is oversimplified. Under pressure, the number of d-electrons increases progressively, initially as a result of a hybridization of the s- and d-bands, which intensifies as the empty d-band approaches the Fermi level and then as a result of the appearance of d-electron pockets at the Fermi surface. The transition of electrons from the s-band to the d-band comes to a complete halt in Cs at about 150 kbar, and in Rb and K at[5,6] 500 and 600 kbar. This process is essentially the reason for the series of phase transitions which are observed in heavy alkali metals. For example, an isostructural transition occurs in Cs when the branch of the d-band with symmetry X_3 begins to fill.[6]

Information on how the electronic structure of alkali metals actually changes during compression can be obtained from optical measurements with diamond anvils. The frequency dependence of the reflection coefficient, $R(\omega)$, in Rb and Cs was studied over a broad pressure range in Ref. 7. Tups *et al.*[7] interpreted their results as evidence of the beginning of a continuous s-d transition in Rb and Cs. However, the functional dependence $R(\omega)$ is a complicated integral characteristic, which does not give direct information on the electronic structure. In order to obtain an unambiguous interpretation of the results of the measurements and thus information on the change in electronic structure, we have carried out "first-principles" calculations of the optical properties of Rb and Cs at the same values of the compression as in Ref. 7. The electronic structure is calculated in a self-consistent way for various values of the lattice constant by a density functional method. The single-frequency electron spectrum $\epsilon_{\mathbf{k}\lambda}$ which emerges from this calculation and also the wave functions $\psi_{\mathbf{k}\lambda}$ ($\mathbf{k}$ is

the quasimomentum, and λ is the zone index) generally describe only the ground state of the system. In metals with delocalized electrons, however, the quasiparticle excitation spectra at low energies $\hbar\omega$ differ only slightly from the spectrum found by the density functional method. This question is discussed in detail in our earlier papers.[8,9] Knowing $\epsilon_{\mathbf{k}\lambda}$ and $\psi_{\mathbf{k}\lambda}$, it is then a simple matter to calculate[8,9] the dielectric constant $\epsilon(\omega)$ and the function $R(\omega)$ in the standard single-particle approximation. To save space here, we will discuss only the results found for Rb at $p = 0$ and 69 kbar. These results do reflect the basic tendencies in the electron spectrum in heavy alkali metals under pressure.

Figures 1 and 2 show the frequency dependence $\epsilon(\omega) = \epsilon_1(\omega) + i\epsilon_2(\omega)$ and $R(\omega)$ at pressures of 0 and 69 kbar, respectively. The dashed lines are experimental curves[7] of $R(\omega)$. Since there are no adjustable parameters in our calculations, we judge the agreement between theory and experiment to be completely satisfactory. In both figures we can clearly distinguish a decay of $R(\omega)$ at $\hbar\omega \approx 4$ eV, which corresponds to the plasma reflection edge ($\hbar\omega_p = 4$ eV). The sharp dip in $R(\omega)$, which is seen at $\hbar\omega \cong 1.8$ eV at a pressure of 69 kbar, is due to another collective excitation of electrons: a so-called collective band mode. As is clear from the curves of $\epsilon_1(\omega)$ and $\epsilon_2(\omega)$, the appearance of an extra zero of $\epsilon_1(\omega)$ at $\hbar\omega \approx 1.8$ eV is due to a sharp intensification of an interband transition [a maximum of $\epsilon_2(\omega)$] at $\hbar\omega \approx 2$ eV. By analogy with the standard terminology, we could call this structural feature in $R(\omega)$ a "quasiplasma" or "band" reflection edge.

With what changes in electronic structure is this intensification of the interband transition associated? Our analysis shows that the interband transition with $\hbar\omega \approx 2$ eV is dominated by electronic states near point N in the Brillouin zone. Figure 3 shows the electron spectrum along the ΓN and ΓH directions at $P = 0$ and 69 kbar. Near

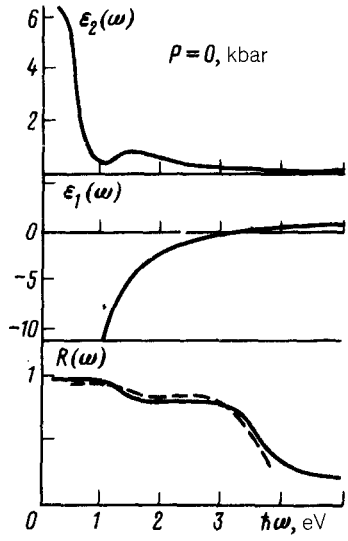

FIG. 1.

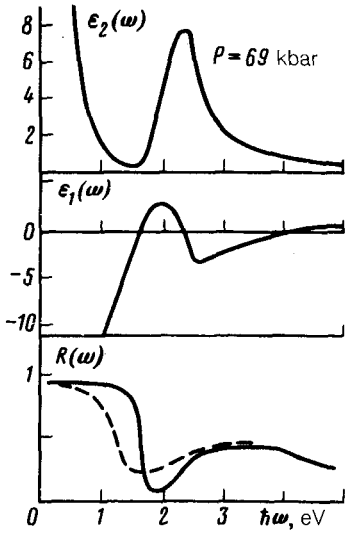

FIG. 2.

point N, the changes in the zone structure are due to the approach of the N_2 level (of d-symmetry) to the Fermi level. This effect intensifies the s-d hybridization, increases the energy gap at the face of the Brillouin zone, and flattens out the spectrum near level N_1. The net result is an intensification of the interband transition at $\hbar\omega \approx 2$ eV under pressure. In contrast with the spherical Wigner-Seitz model, the lowering of the d-band occurs in a very nonuniform way. At $P = 69$ kbar, for example, the d-band comes into actual contact with the Fermi level only at point H (the H_{12} representation), while elsewhere in the Brillouin zone it lies about 2 eV above E_F. At the transition to the fcc structure which occurs at $P = 70$ kbar, the optical properties of Rb change only slightly. In the fcc structure, as in a bcc structure, there is an intense interband trnasition, which leads to a characteristic dip in $R(\omega)$. Here it has an energy of 2.5 eV and is a consequence of excitations of electrons near point L. The results for Cs are extremely similar to those for Rb, but all the effects are shifted down the pressure scale because of the greater compressibility of Cs.

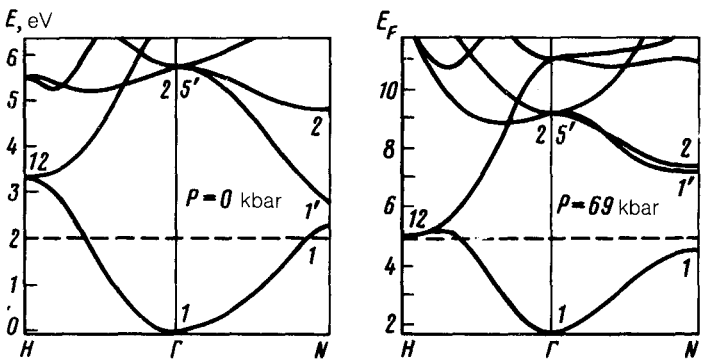

FIG. 3.

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