Interband Optical Conductivity of Potassium*

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The interband optical conductivity of potassium has been calculated in the range 1–10 eV by a first-principles technique. Energy levels, wave functions, and matrix elements were obtained at 2470 inequivalent points in the Brillouin zone from a self-consistent calculation using the method of linear combinations of atomic orbitals. Good agreement with experiment was obtained. An explanation is given for the increased absorption observed in the 5–10-eV range.

Most calculations of the optical properties of the alkali metals have used an independent-particle model of the electron distribution, and have treated the interaction between the electrons and the ions by pseudopotential techniques.[1] Such calculations are usually limited to energies close to the onset of interband transitions. Since there is now no strong reason to believe that many-electron effects are particularly large,[2,3] it seems reasonable to calculate the optical conductivity within the one-electron approximation without using a pseudopotential.

We have made such a calculation for potassium. The results agree rather well with experiment near the threshold for direct transitions. In addition, we are able to account for the increased absorption observed in the 5–10-eV range in terms of our band model.

Our procedure can be summarized as follows. Energy bands and wave functions have been obtained using the method of linear combinations of atomic orbitals (LCAO) as reformulated by Lafon and Lin.[4] This method is quite successful for alkali metals, and our tests show it to be superior to the orthogonalized–plane-wave method unless a large number of waves are employed. The calculation has been carried to self-consistency using an iterative method described elsewhere.[5] The Kohn-Sham formula was employed for the effective exchange potential in an inhomogeneous electron gas. The wave functions were expanded in a basis set consisting of atomic wave functions for the 1s, 2s, 3s, 4s, 2p, 3p, and 4p states expressed as linear combinations of Gaussian-type orbitals as determined by Wachters.[6] We added 3d functions to this set with the aid of Clementi's program. No matrix elements were neglected, and all sums occuring in the Hamiltonian and overlap matrices were carried to convergence. The Hamiltonian matrix has dimensions 18×18. With matrices of this size, it is easy to obtain energies at a large number of points (2470 in $\frac{1}{48}$th of the Brillouin zone). The calculated band structure is shown in certain symmetry directions in Fig. 1.

The real part of the frequency-dependent optical conductivity is given by[1]

$$\sigma(\omega)=\frac{2\pi e^2\hbar}{3m^2\omega\Omega}\sum_{ln\vec{k}}|\langle l\vec{k}|\vec{p}|n\vec{k}\rangle|^2 f_l(\vec{k})[1-f_n(\vec{k})\delta(E_n(\vec{k})-E_l(\vec{k})-\hbar\omega)].$$

In this equation, ω is the frequency of the light, Ω is the volume of the unit cell, and $f_l(\vec{k})$ is the Fermi distribution function for the state $|l\vec{k}\rangle$ (wave vector $\vec{k}$, band l). The matrix elements involved in this formula were computed numerically using the wave functions obtained in the band calculation. The wave-vector dependence of the matrix elements is quite significant. The integration over the Brillouin zone was performed by the Gilat-Raubenheimer method.[7] In addition, an optical effective mass $m_{\text{op}}^*/m = 1.04$ was computed by numerical integration of $|v(\vec{k})|$ over the Fermi surface.

The calculated interband optical conductivity is shown in Fig. 2 (curve a). If a Drude term, characterized by $m_{\text{op}}^*/m_0 = 1.04$ and $\tau = 3.74\times10^{-14}$ sec, is added, the result is curve b. These results are compared with the measurements of Smith,[8] Palmer and Schnatterly,[9] Whang, Arakawa, and Callcott,[10] and Yamaguchi and Hanyu.[11] The agreement is reasonably good. We believe that the large rise in the optical conductivity observed by Whang, Arakawa, and Callcott[10] can be interpreted in terms of the two large peaks found in the calculated conductivity, subject to severe lifetime broadening. The calculated peak around 6.5 eV appears to result from transitions

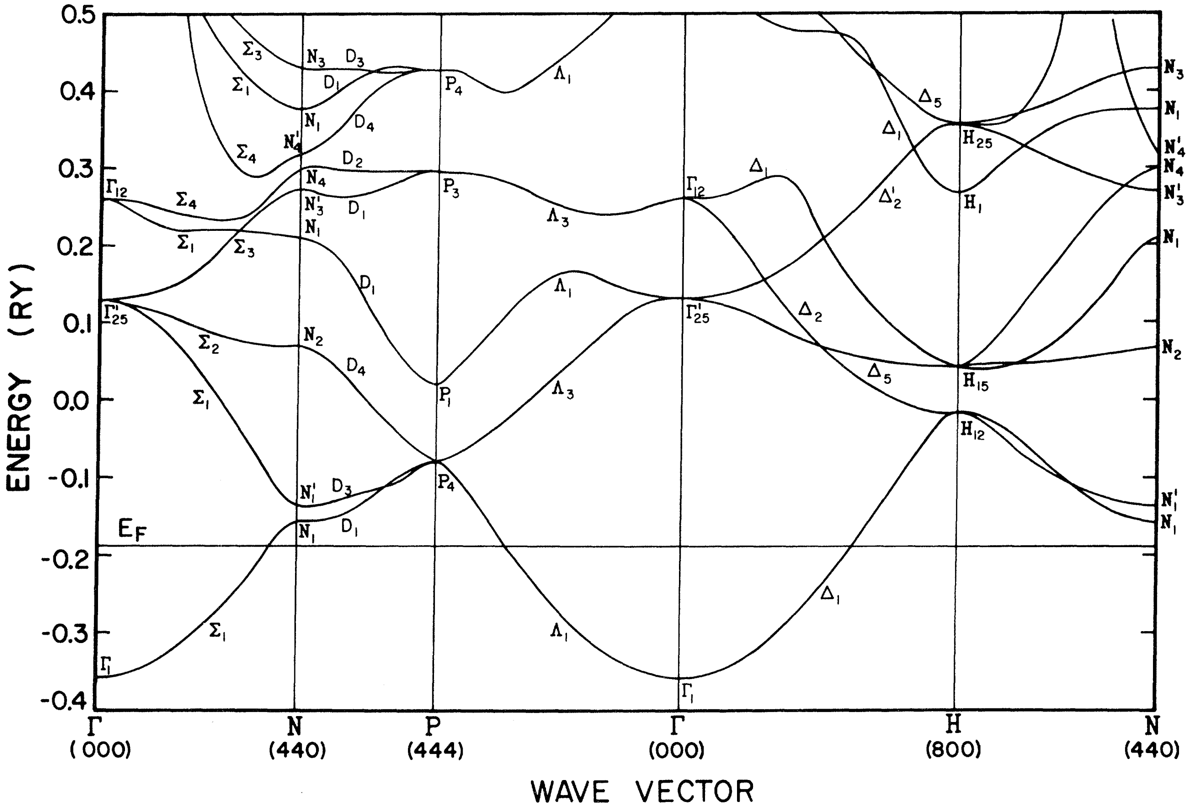

FIG. 1. Energy bands in potassium along some symmetry directions.

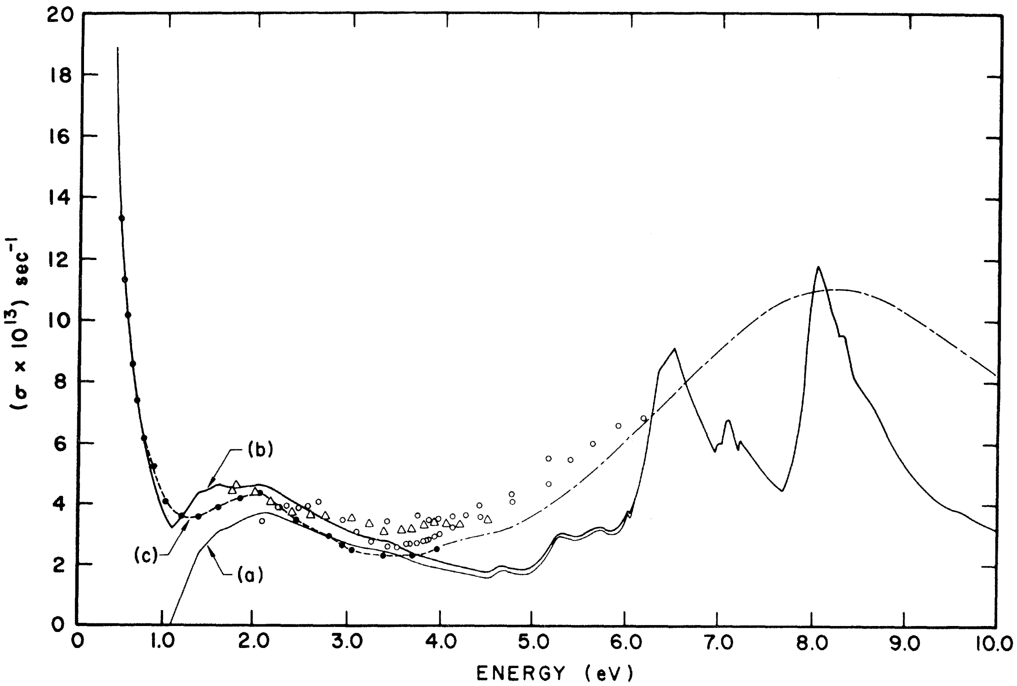

FIG. 2. Calculated and observed optical conductivity of potassium. Curve *a*, interband conductivity; curve *b*, interband plus Drude term; curve *c*, dashes plus filled circles, Ref. 8; dash-dotted curve, Ref. 10; triangles, Ref. 9; open circles, Ref. 11.

between the lowest band and the group of bands emerging from the $\Gamma_{25'}$ level; the peak at 8.1 eV involves the bands originating in Γ_{12}. Although transitions between these states are forbidden at Γ, a substantial contribution results from the mixing of states of different symmetries away from the zone center.

We conclude from these results that band theory enables a reasonably satisfactory description of the low-energy optical conductivity of potassium. There appears to be little need to invoke many-body effects to explain the essential features of the experimental results in the 1–10-eV region.

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Reorientation Kinetics of Fluoride- and Oxygen-Compensated Dipoles in Gadolinium-Doped Calcium Fluoride

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A study of the thermal depolarization spectra for crystals of calcium fluoride containing trivalent gadolinium has been made before and after oxygen contamination. In the oxygen-contaminated crystals, a new ionic thermocurrent peak, with an activation energy of 0.49 eV and a reciprocal frequency factor of 5×10^{-14} sec, is attributed to the relaxation of Gd^{3+}-F^- dipoles in the T_1 complex ($Gd^{3+}O_4^{2-}F^-$).

Although numerous applications of the ionic thermocurrent (ITC) technique[1] to simple impurity-defect dipoles in ionic solids are quite familiar, no relaxations specifically attributable to more complex structures have been reported. We report here for the first time a study of the relaxation of such a complex center, namely, $Gd^{3+}O_4^{2-}F^-$ in calcium fluoride. In addition, earlier work[2] on the relaxation behavior of the tetragonal Gd^{3+}-fluoride interstitial dipolar complex has been confirmed by higher-precision measurements.

ITC refers to the displacement current which results from the thermal release of "frozen-in" polarization as the crystal is warmed at a linear rate. The experimental procedure is to polarize at a temperature T_p at which the dipolar complex of interest can readily reorient, to then cool, with the polarizing field ϵ applied, to a temperature T_0 low enough to "freeze in" the polarization, and then to measure the depolarization current as the crystal is warmed with the field removed. The ITC equation, which gives the form of the ITC curve for a single type of dipole, is

$$j(T)=\frac{N\mu^2\epsilon}{3kT_p\,\tau_0}\exp\left(\frac{-E}{kT}\right)\times\exp\left[-\frac{1}{b\tau_0}\int_{T_0}^{T}\exp\left(\frac{-E}{kT'}\right)dt'\right], \quad (1)$$

where N is the dipole concentration, μ is the dipole moment, τ_0 is the reciprocal frequency factor, E is the activation energy, and b is the heating rate.

In alkaline-earth fluoride crystals containing trivalent lanthanide ions (RE^{3+}), the extra positive charge is usually compensated either by interstitial fluoride ions (F_i^-) or by substitutional O^{2-}. If $CaF_2{:}RE^{3+}$ crystals are grown in reducing conditions with an excess of fluorine, then the predominant dipolar complex is one of tetragonal (C_{4v}) symmetry in which the F_i^- occupies a near-