

CALCULATION OF  $L$  BANDS IN KCl †

L. J. Page,\* J. A. Strozier, Jr.,‡ and E. H. Hygh  
 Department of Physics, University of Utah, Salt Lake City, Utah  
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The absorption cross section for transitions from the  $F$ -center ground state to the conduction band has been calculated for KCl. The absorption bands  $L_1$ ,  $L_2$ ,  $L_3$ , and  $L_4$  are easily identified in the cross section and a new band  $L_5$  has been calculated.

Experimental data concerning the  $L$  bands in alkali-halide crystals have existed for some time,<sup>1</sup> but very little theoretical work has been done. Electrical conductivity experiments suggest that the four absorption peaks which lie to the high-energy side of the  $F$  band and are known as the  $L$  bands result from transition of an  $F$ -center electron directly from the ground state of the  $F$  center into the conduction band. Assuming this model to be correct, we have calculated the dipole approximation to the absorption cross section for such a transition. Comparison with experimental data is quite good.

The dipole approximation to the absorption cross section for a transition from a discrete state (the ground state of the  $F$  center) to a continuum of final states (the conduction-band states) is given by

$$\sigma(\omega) = 4\pi^2 \alpha \omega |\langle f | \vec{r} \cdot \hat{e} | i \rangle|^2 \times \delta(\hbar\omega - [E_k + I]) dn(E_k)/d\omega, \quad (1)$$

where  $\langle f |$  is the final state,  $|i\rangle$  the initial state,  $\omega$  the angular frequency,  $\hat{e}$  the polarization vector of the incident radiation,  $dn(E_k)/d\omega$  the density of final states as a function of their energy  $E_k$ ,  $\alpha$  the fine structure, and  $I$  the ionization energy of the  $F$  center.

The energy bands in the conduction band for KCl were calculated by the interpolation method of linear combination of atomic orbitals due to Slater and Koster.<sup>2</sup> The conduction band was assumed to be made up of  $4S$  and  $4P$  atomic orbitals on the  $K^+$  ions and  $3D$  and  $4S$  atomic orbitals on the  $Cl^-$  ions. The  $4S$  orbitals were placed on the  $Cl^-$  ions following the observation by Oyama and Miyakawa<sup>3</sup> that the potential surrounding the  $Cl^-$  ions seems to be quite spherically symmetric. Interaction between all orbitals was allowed except interactions of the form  $P_x/P_y$ . These were omitted because the exact form of the high-lying  $P$  bands in the conduction band was of little interest in this problem. In matrix elements of the type  $S/D$ ,  $S/P$ , and  $P/D$  only nearest-neighbor interactions were included. The

matrix element  $S/S$  included terms out to fourth-nearest neighbors, while the  $D/D$  terms consisted of the constant term, next-nearest- and fourth-nearest-neighbor interaction terms. The  $P/P$  terms contained the constant term and next-nearest-neighbor interactions. These nine basis functions with interactions contained 25 disposable constants. These constants were determined by least-squares fitting<sup>4</sup> the energy bands to those of the augmented-plane-wave calculation on KCl by DeCicco.<sup>5</sup> The agreement was good to within 0.1 eV over most of the structure but disagreed as much as 0.8 eV for the  $S$ -like band at the  $L$  point. This is on the order of the band-to-band uncertainties of DeCicco's calculation and therefore is consistent with his work.

Having thus determined the 25 constants, the density of states in the conduction band was compiled by calculating the energy bands at 2792 inequivalent points in  $1/48$  of the first Brillouin zone. The results of this calculation are shown in Fig. 1(a).

In order to calculate the transition probability from the  $F$ -center ground state to the conduction band, it is necessary to know the wave function for the electron in the two states. The  $F$ -center ground-state wave function was found by a variational calculation<sup>6</sup> using the semicontinuum model for the potential,

$$V(r) = -\alpha_M/A + W - \chi \quad (2)$$

for  $r < A$  and

$$V(r) = -e^2/Kr \quad (3)$$

for  $r > A$ .  $\alpha_M$  is the Madelung constant,  $W$  a constant to account for the polarization,  $-\chi$  the electron affinity, and  $K$  the effective dielectric constant.  $A$  is the Mott-Littleton<sup>7</sup> radius. The trial wave function used was

$$\psi_{1S} = \frac{\alpha^{3/2}}{(7\pi)^{1/2}} (1 + \beta r) e^{-\beta r}, \quad (4)$$

where  $\beta$  is the variational parameter. This calculation gave a ground-state energy of  $-3.42$  eV.

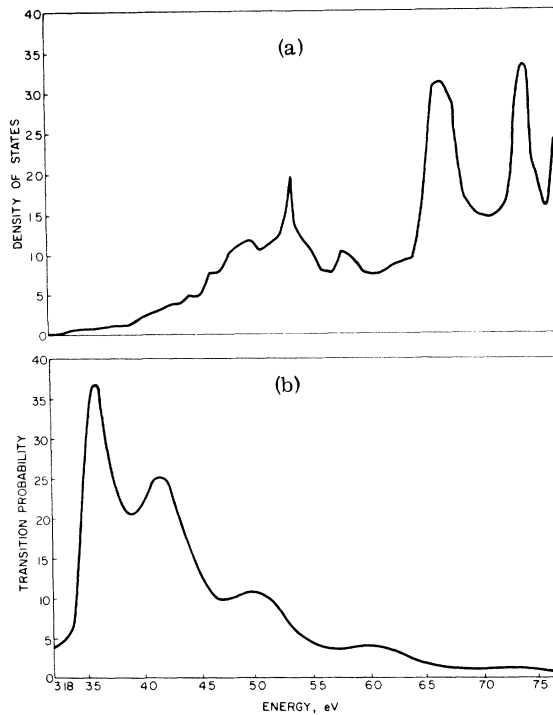


FIG. 1. (a) Density of states in the conduction band for KCl. (b) Transition probability for transitions from the  $F$ -center ground state to the conduction band for KCl.

Krumhansl and Schwartz,<sup>8</sup> using a perturbation approach, have improved on the above model for the polarization and report a value of  $-3.18$  eV for the ground state of the  $F$  center in KCl. The value of  $-3.18$  eV was used for the ionization energy of the  $F$  center,  $I$  in Eq. (1).

An electron in the final state  $\langle f|$  of the system experiences both the  $F$ -center potential and the perfect-lattice potential. Only that part of the final-state wave function near the  $F$ -center defect will contribute to the transition probability because of the highly localized nature of the  $F$ -center ground-state wave function. The  $F$ -center potential is thus much more important than the perfect-lattice potential in finding the final-state wave function. Since the effective mass  $m^*$  in KCl is on the order of 0.6 to 1.0 as shown by Fowler<sup>9</sup> and by DeCicco, the effect of the lattice potential was included by assuming a continuum of final states where  $m^*$  was allowed to take on values from 0.6 to 1.0. No appreciable change in the gross features occurred for these different values of  $m^*$ . Moreover, as DeCicco shows, the higher energy  $S$ - and  $P$ -like states are essentially free electron in character so that a choice of unity is more appropriate for this calculation.

The radial part of the final-state wave function  $U_l(E, r)$  was found by numerically integrating the radial one-dimensional Schrödinger equation

$$\frac{-\hbar^2}{2m^*} \frac{d^2}{dr^2} U_l(E, r) + \left[ \frac{\hbar^2 l(l+1)}{2m^* r^2} + V(r) \right] U_l(E, r) = EU_l(E, r) \quad (5)$$

for positive energies  $E$ . The potential  $V(r)$  was that of Eqs. (2) and (3). Since the  $F$ -center ground-state wave function is an  $S$ -like function, only the  $l=1$  state of Eq. (5) was considered because of the dipole-transition selection rules.

A plot of the transition probability,

$$\left| \int \psi_{1S} r \cos^2 \theta \frac{U_l(E, r)}{r} r^2 \sin \theta dr d\theta d\phi \right|^2,$$

versus the energy is shown in Fig. 1(b). The integral was evaluated numerically. The absorption cross section, the product of the density of states and the transition probability, is shown in Fig. 2.

The absorption cross section contains five large peaks which are identified as the three original  $L$  bands in KCl, the recently discovered  $L_4$  band,<sup>10</sup> and a previously unknown band  $L_5$ . In Table I is shown a comparison of the experimental values for the  $L$  bands and our theoretical values. The width of the energy intervals used in our energy mesh is 0.089 76 eV and thus our values are uncertain to this amount.

Comparison of the absorption cross section with the transition probability and the density of final states shows that  $L_1$ ,  $L_2$ , and  $L_3$  are caused primarily by large peaks in the transition probability. On the other hand,  $L_4$  and  $L_5$  are caused primarily by peaking in the density of final states. The last band,  $L_5$ , would be extremely

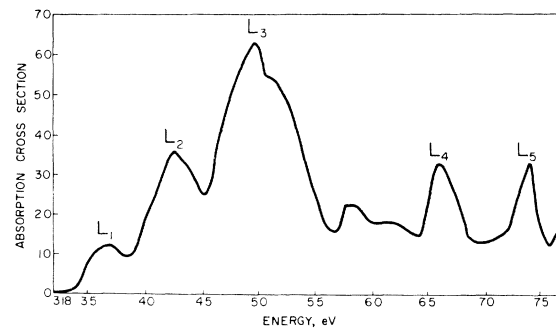


FIG. 2. Dipole approximation absorption cross section for transitions from the  $F$ -center ground state to the conduction band for KCl.

Table I. Comparison of experimental and theoretical values for the  $L$  bands. All values are in units of eV.

	Experiment <sup>a, b</sup>	Theory
$L_1$	3.6	3.63
$L_2$	4.3	4.26
$L_3$	4.95	4.98
$L_4$	6.6	6.60
$L_5$	...	7.40

<sup>a</sup>Ref. 1.

<sup>b</sup>Ref. 10.

hard to identify experimentally because it lies in the region of the absorption spectrum which is dominated by exciton bands and band-to-band transitions.

Work is proceeding to justify the potential used and to calculate other features of the absorption curve of KCl.

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\*National Defense Education Act Fellow 1968-1969.

‡Present address: Material Science and Engineering Department, Cornell University, Ithaca, N. Y.

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## QUANTUM EFFECTS IN CYCLOTRON RESONANCE IN $p$ -TYPE InSb

Kenneth J. Button, Benjamin Lax,\* and C. C. Bradley†

Francis Bitter National Magnet Laboratory, ‡ Massachusetts Institute of Technology, Cambridge, Massachusetts

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Seven cyclotron resonance lines have been resolved providing quantitative data suitable for theoretical analysis of quantum effects of intraband transitions in the degenerate valence bands of indium antimonide. The heavy hole has been resolved for the first time and its mass shows anisotropy. Identification of several transitions with low quantum numbers have been made from observations of their intensities as a function of temperature.

We report the first cyclotron resonance measurements of quantum effects in the degenerate valence bands of indium antimonide. Seven transitions have been recorded by observing the absorption spectra of 0.337-mm monochromatic radiation transmitted through oriented single-crystal specimens of  $p$ -type InSb as a function of magnetic field intensities up to 175 000 G. The magnetic field was applied parallel to the direction of propagation. The lower quantum states of the valence bands were populated by holes thermally excited from an acceptor level. Absorption lines were observed for temperatures between about 20 and 80°K.

The submillimeter spectrometer using an HCN

laser is the same as that described<sup>1,2</sup> for the observation of the quantum effects in germanium except that the cw laser now employs natural gas (methane) and nitrogen as a fuel. A brass light pipe guides the unpolarized laser radiation through an InSb disk which is 2 mm thick. The chopped radiation is detected by a Golay cell and amplified by a Princeton Applied Research Corporation Model-110 tuned amplifier. The doped InSb has a hole mobility of  $7 \times 10^3 \text{ cm}^2 \text{ V}^{-1} \text{ sec}^{-1}$  and impurity concentration of  $6 \times 10^{14} \text{ cm}^{-3}$  measured at 78°K. Such material is available from several commercial sources.<sup>3</sup>

Figure 1 shows the seven resolved transitions observable at this submillimeter wavelength.