$\alpha = A/A_0 - 1$, as

$$pA/NkT = (2/\alpha) + C_0 + C_1\alpha + C_2\alpha^2 + \cdots, \qquad (3)$$

the value of C_0 for the ordinary cell model is $\frac{14}{9}$ = 1.56, for the correlated cell model $\frac{17}{9}$ = 1.89, while the molecular dynamic result gives 1.86 ± 0.03 for either 72 or 870 particles. The values of C_1 are $-\frac{7}{81} = -0.086$, $\frac{62}{81} = 0.765$, and 0.9 ± 0.2, respectively. This quantitative success of the correlated cell model near close packing, as well as in the phase transition, as shown in Fig. 2, indicates its general validity in the high-density region. Figure 2 also shows that for a very steep inverse power-law repulsive potential of the form $kT(\sigma/r)^{100}$ the phase transition disappears. Also, no phase transition was obtained when the repulsive power was four or twelve. For these potentials the integral occurring in the free area of the cooperative cell model was evaluated numerically. A study now in progress involving other potentials,

further models, and three-dimensional systems should help answer the question whether the mechanism of melting in real systems is similar to that of elastic disks.

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OPTICAL TRANSITIONS IN WHICH CRYSTAL MOMENTUM IS NOT CONSERVED*

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Photoemissive studies may give detailed information concerning optical transitions in solids. In particular, the absolute energy of the initial and final states involved in the optical transition can be deduced from the distribution in energy of the emitted electron. Results in good agreement with theory have been obtained from Si.[1] Since optical transitions between valence- and conduction-band states depend on both the energy-band structure and the optical selection rules, photoemission has been used here to obtain information concerning both of these quantities. In Si, in spectral regions of high absorption coefficient and photoemissive yield, only transitions in which $\vec{k}$ is directly conserved are of importance.[1,2] It is the purpose of this Letter to report and discuss data in which no evidence for a selection rule requiring the conservation of $\vec{k}$ was found. The valence-band structure of the materials studied has also been deduced and related to the atomic spin-orbit splitting.

The materials reported on here are IA-VB compounds, Cs_3Bi, Cs_3Sb, Na_2KSb, K_3Sb, and Rb_3Sb which have been rather extensively studied.[3-5] It has been established that photoemission from

these materials is a bulk process. It has also been shown that in many of them a large percentage of the optical transitions produce photoelectrons. The experimental techniques used have been described elsewhere.[6]

If the energy distribution produced by photons of energy $h\nu$ (see Fig. 1) is plotted against the energy of the electron in vacuum, E, minus $h\nu$, the distribution is referred to the valence-band states, at energy E_v, from which it was excited.[7] If only direct optical transitions are important, the energy of the valence-band state from which the electron is excited will change with $h\nu$. As a result, a change in $h\nu$ cannot produce an equal change in E if the valence band has finite width.[1,8] Only if the valence band is flat with negligible width or if the conservation of $\vec{k}$ is not an important optical selection rule, will $\Delta E = \Delta h\nu$. Under these conditions structure in the energy distribution due to the valence band will fall at the same place when the energy distributions for various values of $h\nu$ are plotted versus $E_v = E - h\nu$.

In Fig. 1, experimental energy distributions obtained from Cs_3Bi are plotted versus E_v. For the sake of comparison, the curves obtained for
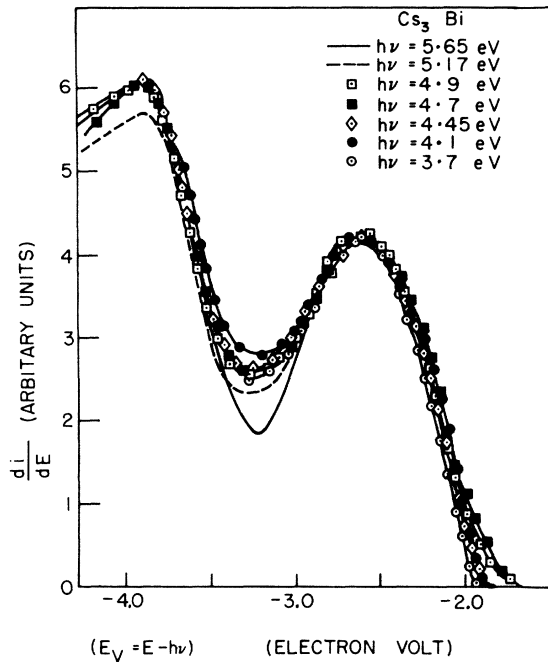
FIG. 1. Energy distributions, di/dE, obtained from Cs_3Bi plotted versus the energy in the valence band, E_v, from which the electrons are excited. Energy is measured from the vacuum level. The values of $h\nu$ indicate the energy of the incident radiation.

FIG. 2. The valence-band density of states of Cs_3Sb and Cs_3Bi showing the spin-orbit splitting. The atomic splitting as calculated by Herman and Skillman (reference 10) is indicated by the arrows. The band widths should be noted; these are about 1.5 eV as compared to about 4.5 eV for Si and Ge [H. D. Hagstrum, Phys. Rev. 122, 83 (1961)].

various values of $h\nu$ were normalized at $E_v = -2.62$ eV. Peaks appear at $E_v = -2.62$ and $E_v = 3.88$ eV for all values of $h\nu$ used. However, the distribution curves have widths of one or two electron volts indicating a corresponding valence-band width. These data can only be understood if it is assumed that the structure in Fig. 1 is due to the density of states in the valence band and that there is no dependence on $\vec{k}$ in the absorption process. We cannot be dealing with an indirect transition involving phonons since the optical absorption is large ($\alpha > 10^5$ cm) and independent of temperature.[9] For the other materials studied here, the peaks in the energy distribution fall at the same value of E_v indicating that conservation of $\vec{k}$ is not an important selection rule. However, the relative magnitudes of the peaks do not always coincide as they do for Cs_3Bi. This is to be expected since the electron escape depth has been found to depend strongly on E for these materials in the energy range of interest.[6]

The observed structure in the valence band in these materials should be due to spin-orbit splitting of the $5p$ antimony or $6p$ bismuth atomic orbitals. The magnitude of the spin-orbit splitting in the solid should be approximately equal to the
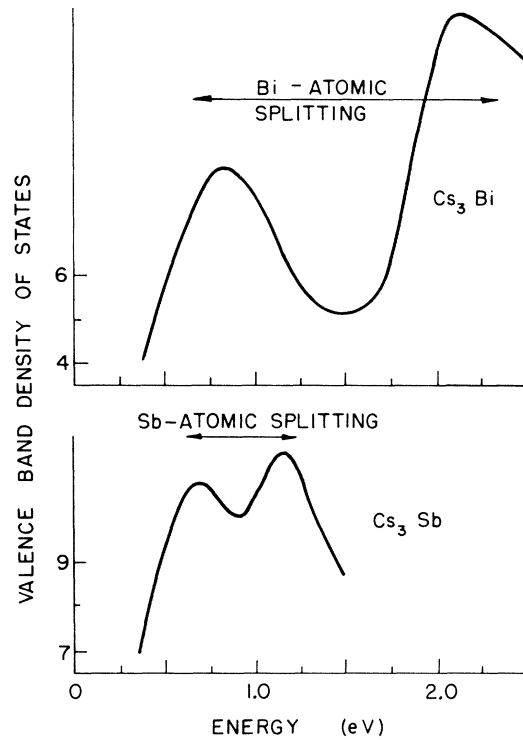
atomic spin-orbit splitting and the multiplicity of the splitting should depend on the crystal symmetry. In crystals with cubic symmetry, the spin-orbit splitting should give two peaks; in crystal not having cubic symmetry, one of these should be broken into a doublet. The experimentally determined densities of states in the valence band for Cs_3Bi and Cs_3Sb which have the same cubic crystal structure are given in Fig. 2. Also indicated are the calculated values of atomic splitting.[10] As can be seen, the experimental and calculated splittings are in good agreement. Notice that both the experimental and calculated splittings increase as one goes from Cs_3Sb to Cs_3Bi. Cs_3Sb, Cs_3Bi, and the other IA-VB compounds which have cubic crystal symmetry show only the two peaks. However, in K_3Sb which has hexagonal symmetry, the higher energy peak has been found by Taft and Philipp[5] to split into a doublet as theory predicts.

The lack of importance of the conservation of

$\vec{k}$ in determining the optical selection rules could only be understood in terms of the conventional one-electron band model if the valence-band states were tightly bound producing narrow bands with high effective masses. Such a situation might be reasonable in these materials due to ionic binding and the fact that the Sb ions from which the valence-band states would be formed are relatively widely separated in the crystal lattice. However, the measured width of the valence bands is much too large (1.0-2.0 eV) for this to be the case. The observed characteristics must then be associated with a very short scattering mean free path which effectively removes the periodicity from the problem.[11,12] Such scattering could result from an extreme amount of misplacement of atoms in the lattice or from extremely close coupling between the valence-band holes and the lattice. The first suggestion seems the least likely since there is no evidence for lattice disorder in the majority of the materials studied,[13,14] and there is evidence that the direction conservation of $\vec{k}$ provides a strong selection rule for pair production.[5,6] If the second suggestion is of importance, it would seem that the Born-Oppenheimer (adiabatic) approximation used in band theory might not hold for these materials.

If the effects described here are due to a breakdown of conventional band theory, other materials which have low-mobility holes (the hole mobility is about 10 cm^2/V-sec in Cs_3Sb) such as the alkali halides and CdS[15] should be expected to exhibit similar characteristics.[12] The energy distribution of the photoelectrons from the valence bands of the alkali halides has been measured by Philipp, Taft, and Apker.[7,16] Their data indicate substantial valence-band widths (1.0 to 2.0 eV) and suggest that direct conservation of $\vec{k}$ is, again, not a strong selection rule. Hole mobility has never been observed directly in the alkali halides. However, the studies of Delbecq, Smaller, and Yuster[17] indicate that in KCl the hole is "self-trapped" due to lattice polarization below -100°C and does not move rapidly at higher temperatures.

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