LOCATION OF THE VALENCE-BAND MAXIMUM IN BISMUTH*

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We note that recent experimental results on the activation energy of electron-hole recombination in bismuth, when combined with recent measurements of the phonon dispersion spectrum, yield the relative separation in momentum space of the valence and conduction band extrema. If we accept the strong experimental and theoretical evidence that the conduction-band minima are at the centers of the pseudohexagonal faces of the Brillouin zone (symmetry points L), our results then indicate that the maximum of the valence band is at the center of the hexagonal face of the Brillouin zone (symmetry point T).

It is now firmly established that the Fermi surface in bismuth can be described by a set of three equivalent, highly eccentric ellipsoids that enclose the conduction-band electrons, and a single ellipsoid of revolution that encloses the holes in the valence band.[1] Since there are only three equivalent electron ellipsoids, crystal symmetry requires that they be centered at either L or X in the Brillouin zone (Fig. 1); similarly the hole ellipsoid must be centered at either T or Γ. Until now, there have been no experimental data that yield either the actual locations of the electron and hole ellipsoids, or their relative position. From the geometry of the zone in Fig. 1, it may be seen that for any combination of the possible locations of the centers of the electron and hole ellipsoids, their relative position in momentum space is equivalent to either the vector ΓX or ΓL. We report here experimental results that show the separation to be ΓX. Thus, if the electron ellipsoids are centered at L, the holes are at T; if at X, the holes are at Γ.

Lopez and Koenig[2] reported the results of measurements of the recombination of electrons and holes in bismuth (electrons scattering from the conduction to the valence band) which indicated that above ~4°K, the recombination is phonon-aided. By increasing the precision of these measurements and extending the range of temperatures at which the data were taken, Lopez[3] has shown (from the activation energy of the recombination rate) that two phonons, of energies 43 ± 4°K and 130 ± 15°K, can each couple the conduction and valence bands.

Smith[4] has extended the earlier measurements of Yarnell et al.[5] on the phonon dispersion relation in bismuth, and computed the appropriate symmetry labeling for the various modes. The phonon energies at the points X and L are shown in Fig. 2 for the three acoustical and three optical mode branches. The phonon energies determined by Lopez are indicated by the hatched areas, where the spread indicates the experimental uncertainty. It is quite clear that the lower energy phonon observed by Lopez can only be an acoustic phonon at X, and not at L, indicating that the centers of the electron and hole ellipsoids are separated by the vector ΓX. The higher energy phonon presumably represents recombination of electrons and holes from these same ellipsoids, aided by optical phonons, judging from Fig. 2. However, since the optical phonon energies are similar not only at X and L, but throughout

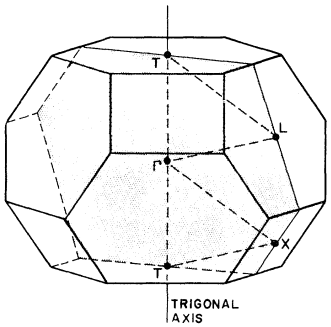

FIG. 1. Brillouin zone of bismuth, showing points of interest to the present discussion. The points T are the centers of the hexagonal faces, L is the center of a pseudohexagonal face, X is the center of a rectangular face, and Γ is the center of the zone. All of these points lie in a mirror plane, shown shaded. The vector TL is equivalent to ΓX, and TX is eqivalent to ΓL.

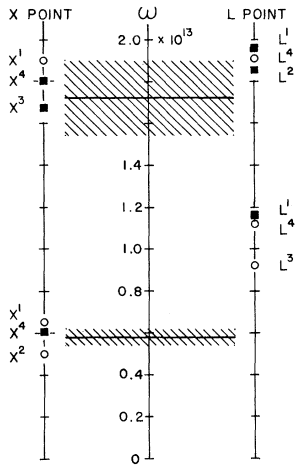

FIG. 2. The phonon energies (in rad/sec) at X and L (Ref. 4) are shown. The hatched areas indicate the energy of the phonons (and the experimental uncertainty) involved in electron-hole recombination (Ref. 3). The data at X and L represented by squares indicate those phonons allowed by symmetry to couple the conduction and valence bands. The data represented by circles correspond to forbidden transitions.

the Brillouin zone,[4,5] the 130°K phonon could also represent interband scattering between other band extrema, were there any well within 130°K of the Fermi level.

There are many theoretical arguments that indicate that the electron ellipsoids are centered at L: the very early arguments of Blount and Cohen[6]; the tight-binding calculations (with spin-orbit interaction) of Mase,[7] and the free-electron results of Harrison.[8] These have been discussed at length by Hall and Koenig,[9] and Cohen, Falicov, and Golin.[10] The most recent work, a pseudopotential band calculation by Golin,[11] concludes that it would take a major alteration of the pseudopotential parameters to put the conduction-band minima at X and still yield the known effective-mass and band-gap parameters, whereas everything fits well for the conduction-band minima at L.

The theoretical position of the valence-band maximum is not as clear. Though the more approximate results of Harrison[8] and Mase[7] show holes at T, the more sophisticated results of Golin[11] are equivocal. In contrast to the theoretical situation for the conduction band, where the energies at X and L are well separated, valence-band maxima occur at both Γ and T with a difference in energy which is within the uncertainty of the calculation.

From the symmetry of the conduction band at L given by Mase[7] and that of the possible valence bands at either T or Γ given by Golin,[11] Lopez[3] has calculated the symmetries of the phonons that will couple the conduction and valence bands, i.e., the phonon-aided electron-hole recombination transitions that are allowed to first order. These phonons are indicated by squares in Fig. 2, in which it may be seen that the experimentally observed phonons correspond to theoretically allowed transitions.

In summary, a combination of the results for the phonon dispersion relation of bismuth with the activation energy of the electron-hole recombination shows that the valence-band maxima and conduction-band minima are separated in momentum space by a vector equivalent to ΓX. If one accepts the experimental and theoretical arguments that the electron ellipsoids are centered at the equivalent L points, our results show that the hole ellipsoid is centered at T.

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SPLITTING OF EXCITON LINES IN WURTZITE-TYPE II-VI CRYSTALS BY UNIAXIAL STRESS*

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Usually the effects of uniaxial stress on exciton lines of semiconductors are considered to be mainly determined by the change of the one-electron energy band structure by the external stress. Energy shifts and splittings of exciton lines are related to the change of energy gaps, effective masses, and degeneracies of the energy bands involved in the exciton state, leading to an interpretation in terms of the deformation potential theory based on the one-electron energy band scheme.[1] In this Letter, however, we report strain-induced splitting of exciton lines observed in the wurtzite-type II-VI crystals, ZnO, CdS, and CdSe, which cannot be accounted for by such a simple deformation-potential theory. The basic features of the experimental results are presented here along with brief discussions on the possible interpretation of the phenomena.

The uniaxial stress measurements have been made on the reflection spectra of oriented samples of ZnO, CdS, and CdSe single crystals at 1.8°K. The force exerted on a parallelepiped sample was generated by a hydraulic system, the details of which will be described elsewhere, and changes of the reflection spectra (for an angle of incidence of about 5°) were measured photographically during uniaxial compression of the sample by a 2-m Bausch and Lomb grating spectrograph with an inverse dispersion of 4 Å/mm. Although measurements have been made for several orientations of the stress relative to the crystallographic axes of the sample, splittings of the exciton lines to be reported here were observed only at the particular geometry where the external uniaxial stress $\vec{P}$ is applied perpendicularly to the C axis and the k vector of the incident light is parallel to the C axis ($\vec{P} \perp C$ and $\vec{k} \parallel C$). For all other geometries, including the case of $\vec{P} \perp C$ and $\vec{k} \perp C$, exciton lines simply shifted in energy but no splitting was observed.

Figure 1 shows the change of the reflection spectra on the (0001) plane of ZnO crystal during uniaxial compression in this particular geometry. A double structure exists initially

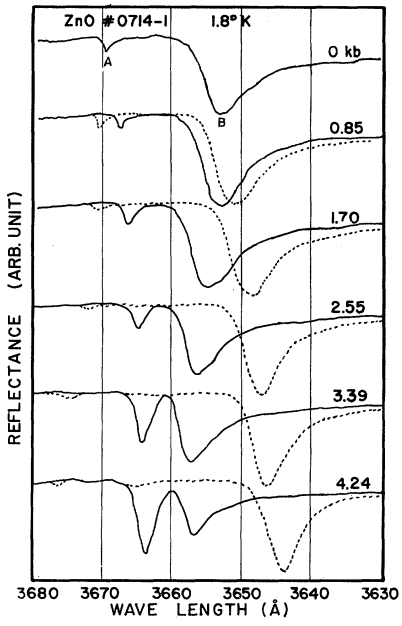

FIG. 1. The change of the reflection spectra of ZnO for $\vec{P} \perp C$ and $\vec{k} \parallel C$. Solid and broken lines indicate the components polarized with $\vec{E} \parallel \vec{P}$ and $\vec{E} \perp \vec{P}$, respectively