BAND STRUCTURE OF GRAY TIN*

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(Received 1 August 1963)

In this Letter a new model for the band structure of α-Sn is proposed which is compatible with the experimental results reported on this material and particularly with the measurements of magnetoresistance and the pressure dependence of the conductivity (σ) and Hall coefficient (R) which have been in relatively poor agreement with models previously suggested.

Theoretical calculations of Herman,[1] and of Liu and Bassani,[2] predict the lowest conduction band to be at the center of the Brillouin zone with Γ_7^- (Γ_2' single group representation) symmetry, and the highest valence band to have Γ_8^+ (Γ_{25}' single group representation) symmetry. This is in agreement with magnetoresistance measurements[3] near 77°K and with oscillatory magnetoresistance data[4] at and below 4°K, both of which show no measurable anisotropy. However, several unrelated measurements require the presence of conduction-band minima of (111) symmetry. Magnetoresistance measurements near 200°K by Tufte and Ewald[3] have shown that this transport property is dominated by electrons in such minima. Pressure measurements of the intrinsic conductivity near this temperature[5] can be interpreted to give a pressure coefficient of an energy gap identical to that of Ge which has a set of (111) conduction-band minima lowest. Measurements of the conductivity, the Hall coefficient, and the magnetic susceptibility as a function of temperature[6] have shown that above 150°K, in samples with impurity concentration of 10^{18}/cc or less, carriers are intrinsically excited with an activation energy of about 0.09 eV. These facts suggest that at 0°K, we might expect the Γ_7^- band to be lowest, with (111), plausibly L_6^+ (L_1 single group representation) symmetry, minima slightly higher in energy.

However, this combination of (000) and (111) bands runs into immediate difficulties. In the first place, the oscillatory magnetoresistance measurements of Hinkley and Ewald yield an effective mass of $0.02 m_0$ with no apparent dependence on carrier concentration. The effective mass of the Γ_7^- electrons can be predicted from the $k\cdot p$ method, if we assume that the main interaction is with the Γ_8^+ (valence) band, that the $\Gamma_7^- - \Gamma_8^+$ energy separation is less than or equal to 0.09 eV, and that the square of the matrix element is 23 eV, which is roughly its value in Ge and InSb. The predicted mass is then more than a factor of three smaller than $0.02 m_0$ and is highly carrier-concentration dependent. In the second place, there is experimental[7] and theoretical evidence[2,8] that the $\Gamma_7^- - \Gamma_8^+$ and $L_6^+ - \Gamma_8^+$ energy gaps should increase with pressure at the approximate rates of 12×10^{-6} eV/bar and 5×10^{-6} eV/bar, and, assuming these coefficients, only the pressure behavior above 200°K is in agreement with the above model.

One clue to the proposed band structure is obtained from a plot of the $\Gamma_7^- - \Gamma_8^+$ energy gap versus λ^2 for the isoelectronic sequence of α-Sn ($\lambda = 0$), InSb ($\lambda = 1$), and CdTe ($\lambda = 2$). λ is a measure of the antisymmetric potential in the lattice, and, as suggested by Herman,[1] this plot should show a linear variation. The line drawn between CdTe and InSb gaps intercepts the $\lambda = 0$ axis at an energy value about 0.2 eV below zero. We should like to point out that this negative gap suggests the model of Fig. 1, and that in terms of this new model the transport measurements are understandable.

In Fig. 1, the Γ_7^- state is placed 0.3 eV below the Γ_8^+ states. The $k\cdot p$ interaction between the

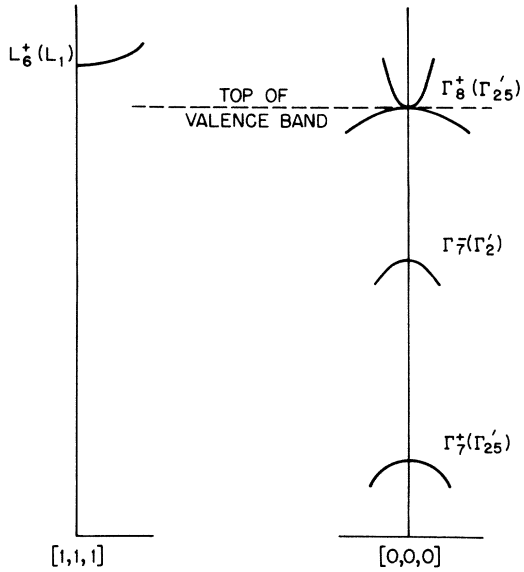

FIG. 1. Energy-band extrema for the proposed model of gray tin.

Γ_7^- and one of the Γ_8^+ levels gives the latter positive curvature. We note first that the energy gap is fixed at zero at all temperatures and pressures. Second, the Γ_8^+-Γ_7^- separation, close to that suggested by the λ^2 plot, is taken to give $0.02m_0$ for the Γ_8^+ conduction-band mass, as measured by Hinkley and Ewald. Third, if the Γ_7^--Γ_8^+ and Γ_8^+-L_6^+ energy gaps retain the pressure coefficients given above, the pressure results are reasonable.

Plotted in Fig. 2 are $\ln R$, $\ln\sigma$, $[R(1\text{ kbar}) - R(0)]/R(0)$ and $[\sigma(1\text{ kbar}) - \sigma(0)]/\sigma(0)$ versus $1/T$ for a sample with roughly 4×10^{15} donor atoms/cc. Intrinsic activation takes place above 20°K for this sample, and the number of electrons in the (111) conduction band is negligible below 90°K. There is evidence that the ratio of electron to hole mobility is sufficiently great below 100°K that R^{-1} will be proportional to the electron concentration. R^{-1} follows a $T^{3/2}$ dependence between 20°K and 90°K, and this is what is predicted for an intrinsic semiconductor of zero energy gap and parabolic conduction and valence bands. Further evidence that the energy gap is tied to zero comes from the observation of the same temperature dependence of R^{-1} at our maximum pressures near 3 kbar, when the energy gap between a Γ_7^- conduction-band minimum and a Γ_8^+ valence-band maximum would have increased by 0.03 eV.

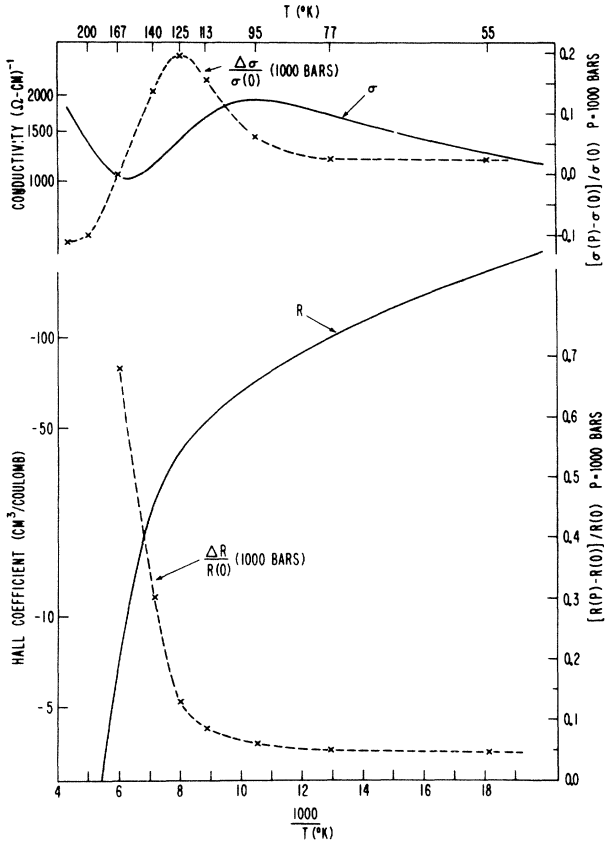

FIG. 2. σ, R, and their fractional changes at 1 kbar versus $1/T$ for a gray tin sample with about 4×10^{15} donor impurities/cc.

If the Γ_7^--Γ_8^+ energy separation decreases with the expected pressure coefficient of 12×10^{-6} eV/bar, the decrease in mass of electrons in the Γ_3^+ conduction band with pressure and the resulting shift in the Fermi level to maintain charge balance gives a predicted 4% increase in R at 1 kbar, in good agreement with a value of 5% observed at 55°K and 77°K.

At the highest temperatures, the large increases of R and large decreases of σ with pressure are consistent with the supposition that the electrons in the L_6^+ minima dominate the transport properties and that the L_6^+-Γ_8^+ energy separation increases with pressure at the same rate as observed in Ge.

A detailed fit of the experimental data to the proposed model in the intermediate temperature region is difficult because a knowledge of the concentration of carriers in all three bands and their relative mobilities is necessary. Taking reasonable values for the effective hole and L_6^+ electron masses, the L_6^+-Γ_8^+ energy separation at $T = 0$°K and its temperature dependence, we have calculated the concentration of carriers in the three bands for various temperatures at atmospheric pressure and 1 kbar. The conditions placed on the relative mobilities when the calculated concentrations and observed R and σ are compared are reasonable. We conclude that this model is in considerably better agreement than any other with the experimental data between 0°K and 160°K.

It should be pointed out that the placing of the (111) conduction-band minima at the boundary of the Brillouin zone is somewhat arbitrary. They have been placed there because of their position in Ge. The arguments presented above do not depend upon the minima being exactly at the zone boundary. It is clear that the model of Fig. 1 would make observation of a sharp absorption edge at Γ_8^+-L_6^+ separation (~0.09 eV) difficult, and it is significant that none has been observed.

We would like to acknowledge helpful discussions with H. Brooks, A. W. Ewald, and G. Peterson.

*This research was supported by the U. S. Office of

Naval Research under Contract Nonr 1866(10) with Harvard University.

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CALCULATIONS OF THE EFFECT OF ORBIT-LATTICE INTERACTION ON THE STATIC SUSCEPTIBILITY AND g FACTOR OF RARE EARTH COMPOUNDS*

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(Received 22 July 1963)

In paramagnetic substances the orbit-lattice interaction has been well known to play an important role in spin-lattice relaxation,[1,2] a dynamic process. We have examined the static consequences of this interaction inasmuch as it yields an additional polarization (or depolarization) of the orbital magnetic moment in the presence of the external magnetic field. Our investigation is mainly of the simple case of a rare earth ion surrounded by a cube of diamagnetic ions. The following approximations are made: (1) The orbit-lattice interaction arises from the linear distortion of the crystal field exerted by the nearest neighbors, which is evaluated on a simple semiempirical point-charge model. (2) A single-ion approximation is used. (3) The lattice vibrations are treated by the Debye model.

We have evaluated the correction to the susceptibility of ytterbium gallium garnet, and to the g shift for Tm^{+2} and Ho^{+2} in CaF_2 at low temperatures. Convergence of the perturbation development is quite good because of the absence of odd-order perturbations in the phonon amplitudes. The correction to the magnetic moment of the ground state is caused entirely by the admixture of excited states through the simultaneous action of both the Zeeman term and the orbit-lattice interaction. At low temperatures this correction arises primarily from the effect of zero-point lattice vibrations and hence is independent of temperature. The temperature-dependent portions, which start with a term in T^4, are negligible below 30°K.

Susceptibility of ytterbium gallium garnet. – Since the next excited level of Yb^{+3} within the $J=7/2$ multiplet is separated by 550 cm^{-1} from the ground level,[3] it suffices to consider only the ground Kramers doublet as populated. The lowest order correction is then given by a third-order perturbation, of the first order in the Zeeman energy and the second order in the orbit-lattice interaction. Neglecting the effect of the excited $J=5/2$ level and the deviation of the static crystal field from cubic symmetry, we find the g shift to be

$$\Delta g = -1.81 \times 10^{-2}.$$

The correction to the second-order Zeeman term comes from a fourth-order perturbation calculation, of the second order both in the Zeeman and in the orbit-lattice interactions. Using the closure approximation which turns out to be very satisfactory, we obtain an energy shift of

$$\Delta E^{(2)}/E^{(2)} = 0.058,$$

where $E^{(2)}$ is the second-order Zeeman energy arising from the nearest quartet. The correction is comparable in order of magnitude with the second-order Zeeman effect arising from admixture of the excited $J=5/2$ multiplet because the Zeeman energy $(\vec{L}+2\vec{S})\cdot\beta\vec{H}$ is nondiagonal in J, and would be observable in the ideal cubic case. In the garnets, uncertainty due to the deviation of the static crystal field from cubic symmetry overshadows our correction and makes its effect on the susceptibility unobservable. If, however, the orbit-lattice coupling were as strong as in the now largely abandoned "fast-relaxing" model,[4] then the susceptibility would be completely altered from its ordinary value.