Piezoresistance in Bismuth

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It is pointed out that the piezoresistance phenomena in bismuth are consistent with some of the multivalley models of bismuth which have been proposed by various authors, and that certain features of these models are in fact implied by the piezoresistance data.

THE electronic properties of bismuth resemble in many ways those of the homopolar semiconductors. These properties have been interpreted[1–6] in terms of multivalley[7] models of the type used for semiconductors, with the top of the valence band being slightly higher in energy than the bottom of the conduction band.

We have recently calculated[8] the elastoresistance effects for a multivalley semiconductor with an axis of rotational symmetry, and in this note we apply the results of this calculation to the piezoresistance measurements of Allen.[9]

We have not reached any conclusions which have not already been suggested by others on the basis of other effects. However, since study of the magnetic effects has not yet established a complete picture of the energy bands, it is of interest to describe the conditions which a multivalley model of the energy bands must satisfy in order to explain the piezoresistance effects.

Cookson[10] has given the piezoresistance tensor for a crystal with the symmetry of bismuth in a coordinate system in which the z axis is the trigonal axis and the x axis is the twofold axis. The tensor has eight independent components, four linear combinations of which can be determined from the results of Allen. These are,[9] in Cookson's notation,

$$\rho_{11}=-7.7, \quad \rho_{13}+\rho_{31}+2\rho_{44}=-9.3,$$
$$\rho_{33}=-6.8, \quad \tfrac{1}{2}(\rho_{14}+2\rho_{41})=13.2,$$

in units of 10^{-9} ohm-cm/(kg/cm^2).

The tensor R_{ij}, which relates the change of resistance to the strain, has a form like that of the piezoresistance tensor. By combining the piezoresistance coefficients of Allen with the measurements of resistivity at high pressures[11] and the elastic constant determination[12] of Bridgman, it is possible to calculate R_{33}. If one calls the resistivity in the z direction r_2, the dimensionless ratio $R_{33}/r_2=20$.

This value 20 for R_{33}/r_2, while not as large as some of the dimensionless elastoresistance coefficients found by Smith[13] for germanium and silicon, is considerably larger than one would expect for a simple model of a metal, and suggests a multivalley semiconductor. However, even in a multivalley semiconductor R_{33}/r_2 is not expected to be large if there is only one band. The reason is that a (zz) component of strain does not destroy any of the crystal symmetry, and cannot therefore remove the energy degeneracy between valleys of the band. It is consequently necessary to assume that carriers from at least two bands make contributions to the electrical conductivity, and that the piezoresistance effect arises from a shift of the energy extrema of one band with respect to another when the crystal is strained.

From Allen's data we can estimate the rate of change of the energy overlap with strain. The dependence of the energy difference between the band extrema on the strain tensor ϵ has the form[8]

$$E=E_0+E_1(\epsilon_{xx}+\epsilon_{yy})+E_2\epsilon_{zz}.$$

E_1 and E_2 can only be found approximately because their relation to the piezoresistance effect depends upon the details of the model of the energy surfaces, the scattering processes and the sample composition. If we assume that the density of states is the same in both bands, that the relaxation time is proportional to (energy)$^{-\frac{1}{2}}$ in each band, and intrinsic material, we find that the (33) component of the elastoresistance tensor is:

$$R_{33}=-\frac{r_2E_2}{2kT(1+e^{E_0/2kT})\log(1+e^{E_0/2kT})}.$$

In this model the Fermi level is $\frac{1}{2}E_0$ above the bottom of the conduction band, so that according to the result of Shoenberg,[3] $E_0/k=420$°K. Using Shoenberg's value of E_0 we find $E_2=3$ ev, a value comparable to those commonly found in semiconductors.[14] The value of E_1 can also be estimated and appears to be somewhat smaller in magnitude than E_2 and of opposite sign. The reasonableness of these magnitudes of E_1 and E_2 lends

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some support to Shoenberg's conclusion that the degeneracy temperature is very small.

The simplest two-band model will not account for all of the observed piezoresistance effects. For if we assume that the extrema of both bands are on the $\mathbf{k}_z$ axis, the energy surfaces are ellipsoids of revolution. about this axis. It can be shown[8] that for such a model the shear coefficient combination $\frac{1}{2}(\rho_{14}+2\rho_{41})$ vanishes. Actually, in bismuth this coefficient has the fairly large value[9] 13.2×10^{-9} ohm-cm/kgcm^{-2}, corresponding to a dimensionless elastoresistance coefficient of about 30. In order to explain this coefficient, it is necessary to assume that at least one of the bands has extrema which are not on the $\mathbf{k}_z$ axis and which, consequently, are at least three in number and are transformed into one another by the symmetry operations of the crystal.

We can thus conclude that a multivalley model of bismuth which explains the piezoresistance effects must have the following features: (1) current carriers from two bands, and (2) one band with a multiplicity of extrema. The magnitude of the effects suggests that the energy difference between the extrema of the two bands is small. A model of bismuth in which the conduction band has three minima and the valence band has one extremum on the $\mathbf{k}_z$ axis has been proposed to explain the de Haas-van Alphen[2-3] and galvanomagnetic effects.[1,4,6]

More extensive experimental study of the piezoresistance effects would be of value in the working out of further details of the energy bands of bismuth. Measurements which completely determine the piezoresistance tensor would allow the elastoresistance coefficients to be calculated and various deformation potential constants to be found. It is difficult to determine parameters of the individual bands from measurements on pure bismuth alone, because the effects are due to both holes and electrons. However, by doping with elements from other columns of the periodic table, materials with conduction by predominantly one type of carrier can be prepared, and piezoresistance studies on such materials would be sensitive to details of the structure of the conduction and valence bands.

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Diamagnetism of Graphite

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The conduction-electron magnetic susceptibility of graphite has been calculated by using the Wallace two-dimensional band structure. The energy levels induced by the magnetic field are calculated by the method of Luttinger and Kohn, taking into account the large (in this case) effects of band-to-band transitions which are not included in the Landau-Peierls treatment. Agreement with the susceptibility observed at high temperatures is obtained with a choice of 2.6 ev for the resonance-integral parameter γ_0. The details of the de Haas-van Alphen effect cannot be reproduced, indicating that a more complicated band structure is needed to account for the low-temperature experiments.

1. INTRODUCTION

THE diamagnetic susceptibility of pure crystalline graphite is large and anisotropic. The difference between the susceptibility parallel to the principal axis and that perpendicular to the principal axis is -21.5×10^{-6} emu/g at room temperature, and the magnitude increases with decreasing temperature.[1] The susceptibility perpendicular to the principal axis[2] is about equal to the free-atom susceptibility of -0.5×10^{-6} emu/g.

Ganguli and Krishnan[1] showed that the temperature dependence of the anisotropic part of the susceptibility is the same as that of a two-dimensional free-electron gas with certain characteristics. Their model has been extended by Mrozowski.[3] However, such a model is not in accord with recent calculations of the electron energy band structure of graphite.[4-6] Further, the work of Hove[7] and the present paper demonstrate that the temperature dependence of the susceptibility is principally due to the Fermi-Dirac statistics.

Several calculations of the susceptibility[7-9] have been made on the Wallace model, using the Landau-Peierls[10] formula for the diamagnetic susceptibility of conduction electrons. The most detailed calculation is that by Hove. He found that though the correct dependences of the susceptibility upon temperature and impurity concentration were obtained, the magnitude of the

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