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The Magnetic Susceptibility of Bismuth Telluride

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Abstract. Measurements of the susceptibility of Bi_2Te_3 over the temperature range 100°K to 600°K, with magnetic field parallel ($\chi_{\parallel}$) and perpendicular ($\chi_{\perp}$) to the c axis, are reported. Bi_2Te_3 is diamagnetic and $\chi_{\parallel}$ has the larger algebraic value.

The contributions to the susceptibility from the core and valence electrons, free carriers and impurities are discussed, and it is suggested that the effect of the impurities is negligible, the free carriers give rise to a paramagnetic contribution and the main contribution is from the core and valence electrons.

§ 1. INTRODUCTION

THE electrical properties of bismuth telluride have been the subject of many recent papers. The transport phenomena have been measured and attempts have been made to explain the results. In particular magnetoresistance measurements have been used to investigate the band structure of Bi_2Te_3 (Drabble, Groves and Wolfe 1958). For a more complete study, measurements of cyclotron resonance would be very desirable. However, it is doubtful if such measurements on Bi_2Te_3 are possible since it is unlikely that specimens having sufficiently low concentrations of charge carriers can be prepared. In the case of germanium, measurements on the magnetic susceptibility have proved useful in the determination of the parameters of the charge carriers and it was considered that similar measurements on bismuth telluride might yield further information on its band structure.

§ 2. EXPERIMENTAL PROCEDURE

Bismuth telluride is anisotropic having a layer type lattice. It is diamagnetic and the susceptibility is also anisotropic. It is therefore possible to measure the susceptibility using the method developed by Krishnan and Banerjee (1935). If a crystal is placed in a uniform magnetic field with c axis horizontal or cleavage planes vertical a couple G acts on it which is given by the formula

$$G = \tfrac{1}{2}(\chi_{\perp} - \chi_{\parallel}) \sin 2\phi \, . \, H^2 m$$

where ϕ = angle between the cleavage planes and the magnetic field H, m = mass of specimen, and $\chi_{\perp}$ and $\chi_{\parallel}$ are the mass susceptibilities with magnetic field perpendicular and parallel to the c axis.

The couple acting on the crystal is a maximum when $\phi = 45°$ and can be measured by suspending the crystal from a quartz fibre. The procedure is to set the torsion head so that initially $\phi = 0$, that is application of the magnetic field causes no rotation of the crystal. The angle through which the torsion head has to be rotated in order to twist the specimen through an angle of 45° is then measured for a known magnetic field. This angle can be accurately measured since the specimen becomes unstable and flips round when rotated through 45°. The quartz fibre can be chosen such that the torsion head is rotated through several revolutions.

In order to obtain the individual susceptibilities it is now only necessary to measure the ratio $\chi_{\perp}/\chi_{\parallel}$. This can be determined by suspending the crystal in a non-uniform magnetic field and measuring the ratio of the forces exerted on the specimen when it is rotated through 90°. The balance described by McGuire and Lane (1949) was used. The magnetic force was balanced by the force between a double coil mounted on the balance arm and a fixed coil, the balance arm being supported by a torsion strip. The electric currents flowing through the coils were measured by a vernier potentiometer and the product of the currents was proportional to the force on the specimen. Four measurements were made by reversing the magnetic field and the currents flowing through the coils. The balance and specimen were contained in a vessel which could be evacuated.

The two methods give $\chi_{\perp}-\chi_{\parallel}$ and $\chi_{\perp}/\chi_{\parallel}$ and observations, say, at room temperature enable the individual values of $\chi_{\perp}$ and $\chi_{\parallel}$ to be calculated. To determine the variation of $\chi_{\perp}$ and $\chi_{\parallel}$ with temperature it was only necessary to use the balance. However as a check, values of $\chi_{\perp}-\chi_{\parallel}$ were determined over the temperature range using the quartz fibre method and compared with values of $\chi_{\perp}-\chi_{\parallel}$ deduced from the other method. The agreement between the two methods was satisfactory.

The magnetic field was produced by an electromagnet designed for experiments on magnetic resonance and consequently had a field which was uniform over a considerable volume. The field was determined using the Hall effect of a specimen of indium antimonide. This specimen had previously been calibrated using the proton resonance method. Temperatures were measured using T_1–T_2 thermocouples. Preliminary measurements of $\chi_{\perp}-\chi_{\parallel}$ on each specimen for different magnetic fields showed no indication of ferromagnetic impurities. Measurements were made on two p-type specimens R 5 and R 8. The electrical properties of these specimens had been measured and are described by Mansfield and Williams (1958). Measurements were also made on an n-type specimen R 9·1. The properties of material adjacent to this specimen in the original ingot have been measured by Williams (1959).

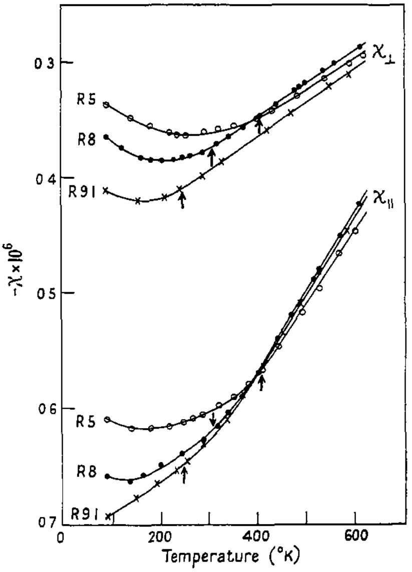
The error likely in the values of the susceptibility at room temperature depends on the accumulation of errors of both methods and is estimated to be 2%. The susceptibility at different temperatures relative to the room temperature values can, however, be determined more accurately.

§ 3. DISCUSSION

The variation of the susceptibilities $\chi_{\perp}$ and $\chi_{\parallel}$ with temperature is shown in the figure. Values of the Hall constant for the different specimens at 90°K are also given. For an account of the transport properties of these specimens reference should be made to Mansfield and Williams (1958) and Williams (1959).

Matyas (1958) has recently determined the susceptibilities of several V–VI compounds and finds for a polycrystalline specimen of p-type Bi_2Te_3 a mass susceptibility of $-0{\cdot}402\times10^{-6}$ which is independent of the temperature. This value is closer to $\chi_{\perp}$ than the average susceptibility obtained in this investigation.

Matyas analyses his results assuming these compounds to be essentially ionic and the contribution to the susceptibility of the free carriers and impurity centres to be negligible. He shows that the susceptibility is proportional to the number of electrons per molecule Z (the values of Z for Bi_2Se_3 and Bi_2Te_3 are given incorrectly and should be 268 and 322 respectively). Such an analysis is useful for discussing the order of magnitude of the susceptibility but cannot explain the anisotropy or temperature variation.



Mass susceptibility of bismuth telluride. Hall coefficients of specimens R 5, R 8 and R 9·1 at 90°K are +0·2, +0·9 and −1·7 cm^3 $coul^{-1}$ respectively.

It was assumed initially that the anisotropy of the susceptibility was due to the free carriers which take part in the transport phenomena and that their contribution could be calculated using the Landau–Peierls formula, the effective masses of the carriers being anisotropic. The following discussion shows, however, that this is not the case.

The measured susceptibility is composed of a number of contributions, χ_L due to core and valence electrons, χ_C due to free carriers and χ_I due to the impurity centres. Reasons will be given later to show that χ_I is negligible and it is only necessary to consider χ_L and χ_C. Now the concentration of charge carriers, and consequently χ_C, varies both with impurity content and with temperature. At a given low temperature the susceptibility decreases in magnitude as the concentration of carriers increases, indicating that the free carriers give rise to a paramagnetic contribution. Because of this it is suggestive to attribute the high temperature linear decrease of the susceptibility to the free carriers, since their concentration increases due to excitation of electrons from the valence band to the conduction band.

This explanation, however, is not adequate. By analysing the variation of electrical conductivity with temperature, it is possible to determine the temperature when the concentration of intrinsic carriers is comparable with the extrinsic carriers. Writing the electrical conductivity as $\sigma = \sigma_i + \sigma_s$ with σ_i and σ_s the contributions due to intrinsic and extrinsic carriers, then the temperatures at which σ_i/σ_s is 10% have been determined for each of the specimens and are shown on the figure by arrows. For temperatures below those indicated by the arrows, the concentration of carriers is constant, while above these temperatures the concentration increases. This increase is relatively slow because the energy gap between valence and conduction bands is small. Now a comparison of the results for the two p-type specimens R 5 and R 8 indicates firstly that, over the temperature range where the concentration of carriers is constant, the difference in susceptibilities of R 5 and R 8 decreases, that is the contribution of the free carriers decreases as the temperature increases. Secondly, in the high temperature range where there is an appreciable temperature variation of susceptibility, a large temperature change is required to alter the concentration of carriers by an amount comparable to the difference of concentration of carriers in R 5 and R 8. Thus the concentration of extrinsic holes in specimen R 5 is three times the concentration of extrinsic holes in R 8. In order to increase the concentration of holes in R 8 by a factor three it is necessary to increase the temperature to 500°K. The change in susceptibility of R 8 as the temperature is increased from 300°K to 500°K is several times larger than the difference in susceptibilities of R 5 and R 8 at 300°K. (It is unlikely that this change is due to the contribution of the electrons produced when the temperature is increased.)

It would appear therefore that the linear decrease in susceptibility at high temperatures is not primarily due to a temperature dependent contribution of the carriers, but due to the core and valence contribution χ_L. A temperature dependence of the susceptibility χ_L of germanium has been observed and Krumhansl and Brooks (1956) have attributed this effect to a Van Vleck paramagnetic term. Because of the small energy gap such a term would be considerably larger in Bi_2Te_3 and would be temperature dependent, since the energy gap varies with temperature. However, it must be noted that the rate of variation of susceptibility is much larger in Bi_2Te_3 than in germanium.

The contribution due to the free carriers, given by the difference in susceptibilities of the different specimens at low temperatures, is much larger than the contribution predicted by the Landau–Peierls formula. Thus the maximum paramagnetic effect given by this formula is $n\mu_0^2/\rho \boldsymbol{k}T$ (μ_0 = Bohr magneton, ρ = density, n = concentration of free carriers). The effect of degeneracy and orbital motion of the free carriers would reduce this quantity. Using values of n given by the Hall constant, this expression gives a contribution which is negligibly small compared with the observed difference in susceptibilities of specimens R 5 and R 8.

This qualitative discussion shows that the main diamagnetic contribution to the susceptibility is from the core and valence electrons and indicates that the valence electrons must exhibit a large Langevin type diamagnetism, the electron configuration being anisotropic. Bismuth telluride has a layer type lattice and similar anisotropy of susceptibility has been observed in other materials with this type of lattice.

The reasons for assuming χ_I is negligible must now be considered. This contribution arises from both the ionized and un-ionized impurities; however it is usual to assume that the effect of the ionized impurities is negligible, especially if they are substitutional impurities. A combination of bismuth and tellurium in the proportion 2 : 3 gives p-type specimens having properties similar to R 5. In order to reduce the concentration of holes or to produce n-type specimens, the starting material is doped with donors, iodine was used in the case of R 8 and R 9·1. The electrical properties show that the concentration of carriers is constant in the extrinsic range, suggesting that the activation energy of the impurity centres is zero or very small. Hence specimen R 5 contains acceptors which are all ionized, R 8 contains donors and acceptors, the former are ionized and a number of acceptors, having the same concentration as donors, are un-ionized. In specimen R 9·1 all the acceptors are compensated and the donors are ionized. It is expected therefore that χ_I will be negligible in the case of specimen R 5, which has all its acceptors ionized, and will be larger for R 8 and R 9·1. The reverse happens in the case of the free carrier contribution χ_C, since the concentration of carriers increases from R 9·1 to R 5. If, therefore, χ_I is responsible for the difference in susceptibility of R 5 and R 8, this contribution must be diamagnetic; if, on the other hand, χ_C is responsible, it must be a paramagnetic contribution. There are two factors which suggest that χ_I is not responsible; firstly, the diamagnetic term for this effect is independent of temperature and one would expect the difference in susceptibilities of the specimens to persist at higher temperatures, whereas the difference decreases until the curves tend to a common intrinsic curve; secondly, the linear dependence of the susceptibility, which appears to be an intrinsic effect, extends to lower temperatures in R 9·1 than R 5, indicating that the impurity contribution is least in R 9·1. This would be the case if the carriers produced by the impurities are responsible for the difference in susceptibilities.

Finally, it should be pointed out that although it has been suggested that the free carriers, in particular the free holes, give rise to a paramagnetic contribution, it is possible that there is a group of electrons having a large diamagnetic effect which is reduced when these electrons are trapped at acceptors or excited to the conduction band to produce the holes.

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