ISSN 1330–0008
CODEN FIZAE4

MAGNETIC PROPERTIES OF SINGLE CRYSTALS OF BISMUTH DOPED WITH GALLIUM AND INDIUM

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Received 2 April 2002; Accepted 20 January 2003
Online 7 February 2003

Diamagnetic susceptibility in single crystals of bismuth doped with gallium and indium has been measured as a function of temperature between 100 and 300 K. Susceptibility decreases with the increase of temperature for each of the samples and also with the increase of the percentage of impurity. An attempt has been made to explain properly the observed phenomena on the basis of the large diamagnetism exhibited by valence electrons.

PACS numbers: 75.20.Ck UDC 537.622.2

Keywords: diamagnetic susceptibility, bismuth doped with indium and gallium, valence electrons

1. *Introduction*

Bismuth, a group-V semimetal, has two overlapping bands. The magnetic property of bismuth has been a subject of interest due to the overlap. Impurities have a considerable influence on the magnetic properties of bismuth. Investigation on the properties of alloys of bismuth is important because various devices are being developed by using alloys of bismuth [1,2]. Several bismuth-containing oxides have been found to be high-T_C superconducting material. Bismuth-antimony alloys have applications in Peltier cooling modules and in infrared detectors. Extensive investigations of the different transport properties of bismuth doped with impurities like lead, tin, tellurium, antimony etc. have been made [3-7]. Investigations with small percentages of impurity were carried out earlier in our laboratory. Reports on bismuth doped with higher percentages of acceptor impurities are scanty. The

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aim of adding higher percentage of acceptor impurity is to deplete the number of electrons in the conduction band and to increase the number of free holes in the valence band. However, doping with higher percentages with lead and tin is not possible [8,9]. Therefore, we have attempted to dope bismuth with indium and gallium whose power of accepting electrons is more than that of lead and tin, and studied their susceptibility as function of temperature. Investigations and analysis of the large diamagnetism exhibited by bismuth and it alloys have been made earlier by several workers [10-17].

Shoenberg and Uddin [11] investigated the magnetic susceptibility χ_c of doped samples of bismuth. In interpreting their observations, it has been found that in addition to large diamagnetism, a paramagnetism also arises due to which diamagnetic susceptibility decreases. Shoenberg and Uddin [11] interpreted the measurements of the de Haas van Alphen effect of bismuth on the basis of a modified theory. They obtained the values of the effective mass components, Fermi energy and density of conduction electrons, and they found that electron ellipsoids occurred with three different orientations. Goetz and Focke [12] also measured the magnetic susceptibility of bismuth doped with different percentages of various impurities. They have suggested that the pronounced effect of small amounts of impurity in bismuth is due to the development of a secondary structure within the single crystals. Blackman [13] and Landau [14] modified the theory of Peierls who originally applied the related theory to a crystal with cubic symmetry only.

Jones [15] used the Landau-Peierls formula to explain the diamagnetic susceptibility of bismuth and its alloys and achieved a good qualitative agreement with the observed temperature variation. According to him, the source of the large diamagnetic susceptibility are the free electrons in the conduction band. Adams [16] suggested that the model developed by Jones [15] required major modification. According to him, when the Brillouin zone is almost filled with electrons and the next upper zone is almost vacant, the sources of large diamagnetism are (i) the filled states near the boundary of the zone and (ii) the unfilled states outside the zone if the values of effective mass for both states are small and the energy difference between states across the boundary of the zone is very small. From the variation of diamagnetic susceptibility with percentage of impurities, Heine [17] is of the opinion that the diamagnetic susceptibility will be reduced if electrons are added to the states outside the zone or are removed from the states inside the zone. According to him, the decrease in diamagnetism with temperature of the samples of bismuth with acceptor or donor impurities is due to the presence of electrons in the conduction band, which is a very strong paramagnetic effect. He also suggested that a filled band has a large diamagnetic contribution when an unfilled band is very near to it with no electrons excited to the upper band. Whenever any excitation to the upper band takes place, the free carriers will have a paramagnetic contribution. Brandt and Razumeenko [18], in order to explain their data on lead doped bismuth, used an idea that strong diamagnetism exists in the valence band of bismuth.

So we find that different authors are not unanimous about the source of large diamagnetism which keeps the substance always diamagnetic in spite of the increasing paramagnetic contribution.

2. *Experiments and results*

Single crystals of bismuth (Bi), doped with indium (In) and gallium (Ga), were prepared in our laboratory by the vertical Bridgeman technique using a modified Bridgeman furnace. Doping bismuth with small percentage of impurity (about 0.1%) leaves the crystal structure practically unchanged [19]. The structure of the samples studied is rhombohedral and it cleaves easily, the cleavage plane being perpendicular to the trigonal axis. The small and thin portions thus cleaved out were cut and then ground into rectangular shapes of dimension 1 cm × 0.3 cm × 0.1 cm for measurements. The percentages of doping of the studied samples, as determined by EDX Analytical System (ISIS Link, Oxford Instruments, U.K.), are given in Table 1.

The magnetic susceptibility ($\chi_\parallel$) of the samples has been determined in the intermediate and the high-temperature range (100 to 300 K) in darkness and in vacuum with the help of a jewel-mounted microbalance developed in our laboratory. The observed temperature variation of $\chi_\parallel$ for the four samples are shown in Fig. 1. The results show that the samples are diamagnetic. The variation of $\chi_\parallel$ with

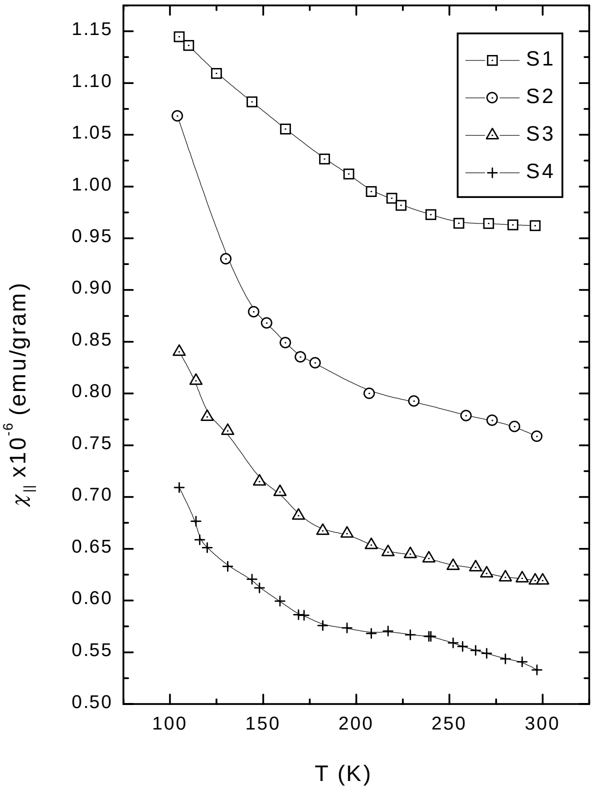

Fig. 1. Temperature dependence of the diamagnetic susceptibility of Bi-In *and* Bi-Ga *alloys.*

TABLE 1. Prepared samples and their percentages of impurity.

Alloy	Sample number	Weighted atomic %
Bi-In	S1	0.008
Bi-In	S2	0.01
Bi-Ga	S3	0.07
Bi-Ga	S4	0.15

temperature is similar in nature for all four samples. The magnetic susceptibility $\chi_{\|}$ decreases with temperature for each of the samples. The value of observed $\chi_{\|}$ decreases at all temperatures as the percentage of acceptor impurity increases.

3. *Discussion and conclusions*

It is known that transport properties of bismuth are exhibited by the carriers in three bands L_{C}, T_{V} and L_{V}, where L and T refer to symmetry points of the Brillouin zone of bismuth. Figure 2 shows a schematic diagram of electron band L_{C} and hole bands T_{V} and L_{V} in a two-dimensional plane. E_{C} is the lowermost available energy level in the L_{C} band and $E_{\mathrm{V}}^{(\mathrm{h1})}$ and $E_{\mathrm{V}}^{(\mathrm{h2})}$ are the uppermost available energy levels in the T_{V} and L_{V} bands, respectively. The Fermi level of pure bismuth, E_{F}^{0}, lies in the region of overlap as bismuth has sufficient number of electrons to fill the band T_{V}. So, in pure bismuth the numbers of holes and electrons are equal at any temperature. Therefore, the system becomes a metal-type system having quasi-continuous energy states above the Fermi level, which are vacant. During the thermal excitation of carriers above the Fermi level, i.e. production of

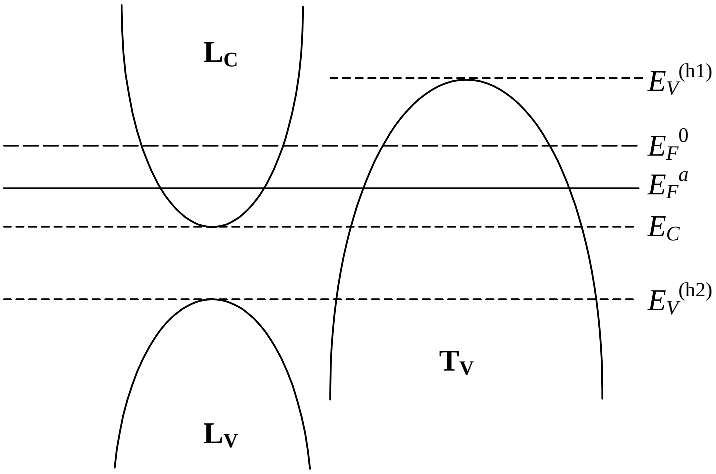

Fig. 2. Schematic diagram of the electron and hole bands.

free carriers, both holes and electrons (in T_V and L_C) will be created. The majority carriers taking part in transport phenomena will be determined by the position of the Fermi level up to which the electrons will occupy the energy states at 0 K. Transport properties of such solids will be exhibited by electrons in the conduction band and holes in the valence bands.

We now try to see what happens to the position of the Fermi level or the number of free carriers when (i) an acceptor impurity is added to pure bismuth and (ii) the temperature of the sample is raised.

(i) In this section we consider the temperature to be fixed at 0 K. We suppose $N_0^{(\mathrm{e})}$ and $N_0^{(\mathrm{h1})}$ are the densities of electrons and holes in bands L_C and T_V in pure bismuth so that $N_0^{(\mathrm{e})}=N_0^{(\mathrm{h1})}$. The position of the Fermi level shifts according to the character and density of the dope. When an acceptor impurity is added, electrons from the bands T_V and L_C will go to the impurity levels and, consequently, the Fermi level will move to the lower energy to a position E_F^a (cf. Fig. 2), and the impurity atoms will be ionized. Now, if $N_\mathrm{i}^{(\mathrm{e})}$ and $N_\mathrm{i}^{(\mathrm{h1})}$ are the densities of the carriers in bands L_C and T_V in the impure sample, and N_a is the density of acceptor impurity centres added to bismuth, then

$$N_\mathrm{i}^{(\mathrm{h1})} + N_\mathrm{i}^{(\mathrm{e})} = (N_0^{(\mathrm{h1})} + aN_\mathrm{a}) + (N_0^{(\mathrm{e})} - bN_\mathrm{a}) \,, \tag{1}$$

where a and b are the fractions of acceptor centres taking away electrons from the bands T_V and L_C, respectively, and are, therefore, proportional to the density of states in T_V and L_C ($a > b$ and $a + b = 1$). The total density of impurities added will be

$$N_\mathrm{imp} = |\Delta N_\mathrm{i}^{(\mathrm{h1})}| + |\Delta N_\mathrm{i}^{(\mathrm{e})}| \,, \tag{2}$$

$$\Delta N_\mathrm{i}^{(\mathrm{h1})} = N_\mathrm{i}^{(\mathrm{h1})} - N_0^{(\mathrm{h1})} \quad \text{and} \quad \Delta N_\mathrm{i}^{(\mathrm{e})} = N_0^{(\mathrm{e})} - N_\mathrm{i}^{(\mathrm{e})} \,.$$

From the above argument, it is clear that there will be an increase in the total number of carriers (electrons + holes), but the increase will be less than the total number of impurity centres added.

If the concentration of impurity is increased, the impurity will take more electrons from the bands, and after a sufficient percentage of impurity, the Fermi level E_F^a moving to the lower energy may enter into the region of the L_V band. As a result, more holes will be created in T_V and L_V bands and L_C band will be devoid of electrons. The above expressions relate the concentration of impurities and the number of free carriers with the consequent shift of the Fermi level.

(ii) As the temperature rises, electrons from T_V and L_V will be excited to higher states. Excitation of electrons from one valence band to the other valence band has also been considered, as has been done previously by workers of this laboratory [10,20–22].

If a very small amount of acceptor impurity is added, the Fermi level may remain within the overlap region. As the temperature is raised, electrons from T_V will go to the vacant states in L_C, thereby increasing the number of free electrons in L_C, and the same number of holes will be created in the band T_V. From L_V, excited electrons will go to both T_V and L_C. Electrons that go to the vacant states in T_V decrease the number of holes in T_V and those going to L_C increase the number of free electrons. Also, the total number of electrons excited from L_V will give rise to the same number of holes in L_V. At any certain temperature, if N_1 and N_2 be the densities of electrons excited from T_V and L_V bands, respectively, the density of carriers in the respective bands will be

$$\begin{aligned} \text{holes in } T_V, \quad N^{(\mathrm{h1})} &= N_\mathrm{i}^{(\mathrm{h1})} + N_1 - pN_2 \,, \\ \text{holes in } L_V, \quad N^{(\mathrm{h2})} &= N_2 \,, \\ \text{electrons in } L_C, \quad N^{(\mathrm{e})} &= N_\mathrm{i}^{(\mathrm{e})} + N_1 + qN_2 \,. \end{aligned} \tag{3}$$

Here p and q are the fractions of N_2 going to the vacant states of T_V and L_C, respectively. The values of p and q depend on the vacant states available and their positions in T_V and L_C; $p + q = 1$. N_1 and N_2 can be calculated as a functions of temperature using the Fermi-Dirac distribution function $f(E)$,

$$N_\mathrm{i} = \int_E^{E+dE} g(E')f(E')\mathrm{d}E'; \quad g(E') = \text{density of states at energy } E' \,.$$

If the Fermi level lies in the region of band gap due to a increase in the amount of acceptor impurity, the density of carriers in the respective bands at any certain temperature will become,

$$\begin{aligned} \text{holes in } T_V, \quad N^{(\mathrm{h1})} &= N_\mathrm{i}^{(\mathrm{h1})} + N_1 - pN_2 \,, \\ \text{holes in } L_V, \quad N^{(\mathrm{h2})} &= N_2 \,, \\ \text{electrons in } L_C, \quad N^{(\mathrm{e})} &= N_1 + qN_2 \,. \end{aligned} \tag{4}$$

So we find from Eqs. (3) and (4) that in both above cases, the total number of carriers increases with temperature.

On the basis of the above proposition, we now try to account for the observed variation of $\chi_\parallel$ with temperature. The explanation is qualitative in nature. Our observations are confined to the intermediate and higher region of temperature (100–300 K). It is known that the diamagnetic susceptibility is given by

$$\chi = \chi_\mathrm{L} + \chi_\mathrm{i}(0) + \chi_\mathrm{i}(T) + \chi_\mathrm{C}(T) \tag{5}$$

where χ_L is the temperature-independent contribution from core electrons and electrons in the valence band [23], $\chi_\mathrm{i}(0)$ the temperature-independent contribution to the susceptibility from any neutral impurities that may be present, $\chi_\mathrm{i}(T)$ the temperature dependent susceptibility due to paramagnetic impurities (if any) and $\chi_C(T)$ the magnetic susceptibility due to free carriers.

According to Adams [16], χ_L of Eq. (5), which is taken to be temperature independent, has a contribution of the same order as that of χ_C. As stated above, χ_L is the result of the diamagnetic contribution of the core electrons and the valence electrons. The valence electrons concerned here are those which are not free carriers. Therefore, the temperature-independent diamagnetic susceptibility will be proportional to the number of such electrons in the valence band. According to Adams [16] and Heine [17], these electrons will contribute a large diamagnetism if there is an upper vacant band with a very small energy gap when the states in both these bands have small effective mass. When thermal excitation of electrons from valence bands (L_V and T_V) to conduction band (L_C) takes place, there will be a decrease in the number of valence electrons in bands L_V and T_V. Therefore, we have to consider the following two effects:

(a) Free electrons thus excited in the conduction band (L_C) and holes in the valence bands (L_V and T_V) will contribute to magnetic susceptibility according to the Landau-Peierls formula,

$$\chi_C(T) = \frac{N\mu_B^2(3-\alpha^2)}{3kT}$$

where N is the density of free carriers at temperature T, μ_B the Bohr magneton, k the Boltzmann constant and α is the ratio of the rest mass to the effective mass of the carriers.

(b) A decrease in the diamagnetic susceptibility due to a decrease in the number of valence electrons (in bands L_V and T_V) since the valence electrons contribute a large diamagnetism. This means that χ_L, which is generally thought to be temperature independent, is not so.

In bismuth, the band gap is $E_g \sim 0.015$ eV [3,4,7] so that with the increase of temperature, the number of free carriers N increases and hence the value of $\chi_C(T)$, which depends on N/T, will also increase. But in the samples studied, no increase of the value of $\chi_\parallel$ was observed in the range of temperature investigated (100–300 K), instead a decrease was observed. It is known that the large diamagnetism of bismuth is due to the large diamagnetic contribution of the core and valence electrons. This decrease can be explained if we consider the argument given above that χ_L decreases as electrons from the valence band are thermally excited. Since χ_L is large, the contribution of each electron in the valence band is also proportionately large and is larger than the diamagnetic contribution which this same electron makes when excited to the upper band as free carrier. This follows from Morimoto and Takamura's calculations. Morimoto and Takamura [7] calculated the diamagnetic susceptibilities ($\chi_\parallel$ and $\chi_\perp$) of the free carriers of pure bismuth knowing the values of N and α and found that the calculated value is much too small, about 1/50 to 1/100 of the experimental values. They have found that the calculated value is much less than the experimental value in the case of 0.2 at% tin-doped bismuth. The decrease in the observed $\chi_\parallel$ mentioned above, therefore, doesn't seem to be due to any increase of the paramagnetic contribution of carriers. The percentage of impurity for the sample S1 (mentioned in Table 1) is small so that the Fermi level may lie within the overlap region. Then a significant amount of excitation of electrons from the T_{V} band to L_{C} band takes place in the intermediate temperature range. The Fermi level moves to lower energy with the consequent increase of the amount of impurity. With the shift of the Fermi level to a lower energy, the excitation of electrons from T_{V} to L_{C} starts at a higher temperature, but excitation from L_{V} to T_{V} starts at a lower temperature. Morimoto and Takamura [7] have also shown that the diamagnetic susceptibility due to heavy holes is far smaller than that of light holes. So, due to the decrease in the number of valence electrons in L_{V} band, the decrease in the diamagnetic susceptibility is more than compensated by the diamagnetic contribution of the same number of valence electrons excited to T_{V} band. Therefore, for the sample S1 with a low amount of impurity, in the intermediate-temperature range, the decrease in $\chi_{\|}$ is due to the excitation of electrons from T_{V} band, and in higher-temperature range the decrease is due to the excitation from both L_{V} and T_{V} bands. We may conclude that with the consequent increase of the percentage of impurity, the thermal excitation of electrons from L_{V} becomes important in decreasing $\chi_{\|}$ with temperature. Therefore, as more electrons are excited due to a rise of temperature, the diamagnetic susceptibility $\chi_{\|}$ will decrease. This is illustrated by the observed temperature variation of $\chi_{\|}$ for the samples S2, S3 and S4 in Fig. 1. It must be remembered that though χ_{L} is showing a temperature dependence, it is not so for free carriers. In the case of free carriers, even if the number of free carriers is fixed, $\chi_{\mathrm{C}}(T)$ decreases as $1/T$. But for a fixed number of core and valence electrons, χ_{L} is temperature independent. Here the decrease of χ_{L} is due to the decrease in the number of electrons in the valence band. In other words the susceptibility per electron in χ_{L} is temperature independent. That χ_{L} sometimes shows a temperature dependence has also been observed in germanium [24]. Thus the proposition given above can explain the decrease in $\chi_{\|}$ with temperature.

The decreases in $\chi_{\|}$ with the amount of impurity can also be accounted for with the above-discussed argument. With the increase of acceptor impurity, the number of electrons decreases from both conduction band and valence band. The decrease of $\chi_{\|}$ with the percentage of impurity is mainly due to the decrease in the number of valence electrons in the valence band because these electrons contribute a large diamagnetic susceptibility. Thus all the features in the observed diamagnetic susceptibility $\chi_{\|}$ of bismuth doped with indium and gallium can be explained by the proposed model.

Acknowledgements

The authors D. Bannerjee and R. Bhattacharya acknowledge the financial support of the University Grant Commission. They wish to thank the authority of Indian Association for the Cultivation of Science, Jadavpur, Kolkata for providing with the facilities of the laboratory. The authors are also thankful to Prof. A. K. Pal of the Department of Solid State Physics for his kind interest in the work and the help extended to us.

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MAGNETSKA SVOJSTVA MONOKRISTALA BIZMUTA PUNJENIH GALIJEM I INDIJEM

Mjerili smo dijamagnetsku susceptibilnost monokristala bizmuta punjenih galijem i indijem u ovisnosti o temperaturi između 100 i 300 K. Susceptibilnost se smanjuje s povećanjem temperature i povećanjem punjenja za sve uzorke. Predlažemo tumačenje postignutih ishoda mjerenja na osnovi jakog dijamagnetizma koji pokazuju valentni elektroni.