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N-Type Behaviour in Acceptor Doped Bismuth

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Abstract

Hall coefficient of bismuth single crystal doped with gallium has been measured in the temperature range 100 - 300K for different magnetic field strengths. Gallium is an element of group III and so it should act as an acceptor impurity to bismuth. The Hall coefficient is expected to be positive. However, the coefficient is observed to have negative sign in most cases. Change of sign of the coefficient is also observed for higher magnetic field strengths

Keywords: Hall coefficient, Bismuth

Introduction

Bismuth is a semimetal which plays an important role in solid-state physics. It has a small valence and conduction band overlap, three small L point electron Fermi pockets, and a T point hole Fermi pocket, which gives an equal (small) number of both charge species at the Fermi level.[1] L and T refer to symmetry points of the Brillouin zone of bismuth. The band structure of pure bismuth may be considered to consist of a pair of light mass bands (L_C for electrons and L_V for holes) at six symmetrically related positions in **k**-space (six half ellipsoids) and a heavy mass hole band(T_V) at two positions in **k**-space (two half ellipsoids). The six half ellipsoids for each of the electrons and holes in the Brillouin zone may be considered as three whole ellipsoids centered at L-point and two half ellipsoids for the heavy holes as one whole ellipsoids centered at T-point. It is therefore a two-carrier system. The electrical transport properties of bismuth and its alloys have been a subject of interest due to the overlap. Bismuth has an extremely small Fermi surface. So this material provides the remarkable possibility to observe strong effects induced by the presence of impurity. Extensive investigations of the transport properties of bismuth doped with impurities like lead, tin, tellurium, antimony etc have been made.[2-6] In the last few years, a series of experiments has once again drawn the attention of the community to elemental bismuth and challenged our understanding of this material. The recent experiments clearly indicated that the question of transport in bismuth was still not understood.[7] In fact, similar questions still existed for the standard resistivity as well. A material of much long term interest with many interesting properties bismuth has recently been found to host a variety of exotic electronic phenomena, including phase transitions at high field.

Bismuth has a rhombohedral crystal structure with two atoms per unit cell one at (u, u, u) and the other at (-u, -u, -u) with respect to lattice vectors, where u=0.237. The lattice vectors are $|a_1|=|a_2|=|a_3|=4.74$Å and are at an angle $\alpha=57.23$ degrees to one another.[8] The structure of bismuth would be cubic if α were 60 degrees, so one may consider bismuth as having a slightly distorted cubic lattice. The crystallographic axes, usually referred to as the binary, the bisectrix, and the trigonal or c-axis, pertaining to the x-, y-, and z-axes respectively. The unit cell contains two atoms situated on the trigonal body diagonal at 23.4 and 76.6 per cent of its length.

There has been extensive interest in the transport properties of bismuth because of its unusual behavior that is exhibited due to the low density and very high mobilities of carriers. Bismuth behaves like a metal though not strictly metallic. Its behavior is in between a metal and a semiconductor. Both holes and electrons are found to be responsible for the transport properties.

The purpose of this work is to reexamine the transport properties of doped semimetal. We present in this article the results of Hall coefficient study of gallium doped bismuth single crystal.

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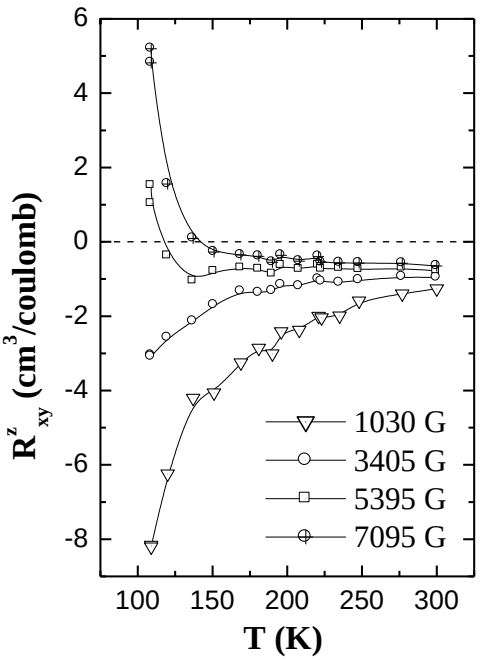
Experiments and Results

Single crystal of bismuth doped with gallium was prepared by the vertical Bridgeman technique using a modified Bridgeman furnace. The percentage of doping of the studied samples, as determined by EDX Analytical System (ISIS Link, Oxford Instruments, U.K.) is 0.22 weighted atomic percent. The current was applied in the direction perpendicular to the trigonal axis and magnetic field was applied parallel to the trigonal axis.

Figure 1 shows the temperature variation of Hall coefficient (R^z_{xy}) of the sample. The Hall coefficient is found to be negative throughout the range of temperature investigated (100-300K) for the two low magnetic field strengths. The negative value increases as the temperature is lowered. For higher field strengths a change of sign of the coefficient is also observed in the low temperature region.

Fig. 1 Temperature Variation of Hall Coefficient of 0.22 At% Gallium Doped Bismuth. Applied Magnetic Field Strengths Are Indicated in the Figure



Discussion

Various types of band calculation have been carried out for bismuth, pseudopotential techniques are most common. The effect of rhombohedral distortion on which the energy band model of bismuth is based, is to lower the bands at the L-point and to raise them at T-point. This causes small overlap at L and T points. According to some workers the overlap is vertical [9-11]and according to some others it is not.[12] The surfaces which contain point T are regular hexagons unlike the surfaces with the point L which are not regular and are called pseudohexagonal. Bismuth is pentavalent and from the two atoms in the unit cell ten valence electrons originate. They would fill a whole number of bands if a slight band overlap did not occur. Due to this overlap a few electrons are accumulated in the next-higher band, leaving an equal number of holes in a nearly filled band. Both these electrons and holes act as free carriers. The wave vectors **k** of these holes and electrons are all located in valleys near boundary planes of the Brillouin zone around the points L and T respectively.[13,14] For many cases a satisfactory representation of the band structure over a restricted region of **k**-space is achieved in terms of two coupled bands. Based on infrared transmission experiments[15], Lax[16] proposed an ellipsoidal-non-parabolic model for the Fermi surface of bismuth which has been found to work quite well in explaining physical properties.

One axis of each electron ellipsoid is parallel to a crystallographic axis (binary axis having 1 or x), the other two axes of each ellipsoid are tilted with respect to the other crystallographic axes (trigonal axis having 3 or z and bisectrix axis having 2 or y). According to the relation of energy versus wave-vector proposed by Lax, the electron ellipsoids can be described as

$$E_e\left(1+\frac{E_e}{E_g}\right)=\frac{\hbar^2}{2m_0}\left(\alpha_{11}^{(e)}k_x^2+\alpha_{22}^{(e)}k_y^2+\alpha_{33}^{(e)}k_z^2+2\alpha_{23}^{(e)}k_yk_z\right)$$

where E_e is the electron Fermi energy, E_g is the band gap between the two light mass bands(L_C and L_V), and $\alpha_{ij}^{(e)}$ the components of reciprocal electron mass tensor $\boldsymbol{\alpha}^{(e)}$ in unit of ($1/m_o$); m_o being the free electron mass. This is known as the Lax or ellipsoidal-non-parabolic model. The three light hole ellipsoids are also of the same form as the three electron ellipsoids described above. The Fermi surface of heavy hole is described by one set of ellipsoid with its axis of revolution parallel to the trigonal axis. The ellipsoid of revolution for heavy hole is of the form

$$E_{h1}=\frac{\hbar^2}{2m_0}\left(\alpha_{11}^{(h1)}\left(k_x^2+k_y^2\right)+\alpha_{33}^{(h1)}k_z^2\right)$$

where E_{h1} is the heavy hole Fermi energy and $\alpha_{ij}^{(h1)}$ is the components of reciprocal heavy hole effective mass tensor $\boldsymbol{\alpha}^{(h1)}$.

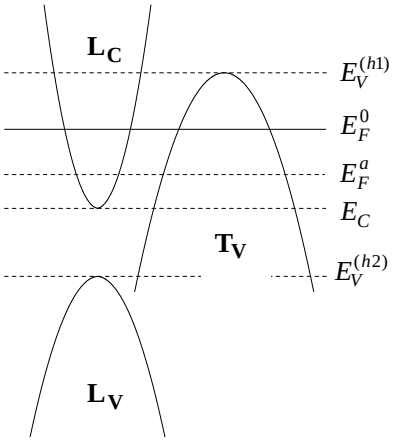


Fig. 2 Schematic Diagram of the Electron and Hole Bands.

Figure 2 shows a schematic diagram of energy bands in bismuth showing a projection of energy bands L_C, T_V and L_V on a two-dimensional plane. E_C is the lowermost available energy level in the L_C band and

$E_V^{(h1)}$ and $E_V^{(h2)}$ are the uppermost available energy levels in the T_V and L_V bands respectively. As bismuth has sufficient number of electrons to fill the band T_V, we get a Fermi level E_F^0 in the region of overlap due to the distribution of electrons among the energy states of T_V and L_C in the that region. L_C and L_V bands will give rise to light mass electrons and light mass holes respectively as free carriers and the T_V band to heavy mass holes. When an acceptor impurity is added to bismuth the impurity takes electrons from both the overlapping bands, thereby increasing the number of holes and decreasing the number of electrons. The Fermi level then moves to a lower energy to a position E_F^a.

The theoretical three band model for pure as well as doped bismuth predicts the Hall coefficient in the xy-plane with the magnetic filed H along z-axis as

$$R_{xy}^z = \frac{\frac{1}{e} \times A_1}{A_1^2 H^2 + A_2^2}$$

where the following two terms are taken as A_1 and A_2 in the above expression of R_{xy}^z,

$$\frac{N^{(h1)}\mu_1^{(h1)^2}}{1+\mu_1^{(h1)^2}H^2} + \frac{N^{(h2)}\mu_1^{\{h2\}}\mu_2^{\{h2\}}}{1+\mu_1^{(h2)}\mu_2^{(h2)}H^2} - \frac{N^{(e)}\mu_1^{\{e\}}\mu_2^{\{e\}}}{1+\mu_1^{(e)}\mu_2^{(e)}H^2} = A_1$$

$$\frac{N^{(h1)}\mu_1^{(h1)}}{1+\mu_1^{(h1)^2}H^2} + \frac{N^{(h2)}\overline{\mu}^{(h2)}}{1+\mu_1^{(h2)}\mu_2^{(h2)}H^2} + \frac{N^{(e)}\overline{\mu}^{(e)}}{1+\mu_1^{(e)}\mu_2^{(e)}H^2} = A_2$$

Here $\mu_1^{(h1)}$ is the (isotropic) mobility of heavy holes in the xy-plane, $\mu_1^{(e)}$ and $\mu_2^{(e)}$ are the electron mobilities taken for each electron ellipsoid in the xy-plane and $\mu_1^{(h2)}$ and $\mu_2^{(h2)}$ are those for light holes respectively. $\overline{\mu}^{(e)}\left(=\frac{\mu_1^{(e)}+\mu_2^{(e)}}{2}\right)$ and $\overline{\mu}^{(h2)}\left(=\frac{\mu_1^{(h2)}+\mu_2^{(h2)}}{2}\right)$ are the average mobilities of electrons and light holes in the xy-plane respectively.

The mobility of a charge carrier is in general determined by collision of the carriers with lattice vibrations (phonons), ionized impurities and neutral impurities, dislocations, vacancies and interstitials. Of these the first one happens to be the most important in case of crystals.

The mobility associated with scattering due to lattice vibrations for non-polar crystals varies as $T^{-3/2}$. Experimental observations however are not always in precise accord with this formula.

When the concentration of ionized donors or acceptors is high, the charge carriers suffer Rutherford scattering due to the presence of such ions. The characteristic of the ionized impurity scattering is the approximate power law

$$\mu \propto T^{3/2}$$

The two important factors responsible for the temperature variation of mobility are phonons and ionized impurity atoms. We consider that the three groups of carriers stand in the same ratio when scattered by phonons and the impurity ions. Any arbitrary carrier mobility, when scattering mechanism occurs independently, is determined by

$$\frac{1}{\mu} = \frac{1}{\mu_{imp}} + \frac{1}{\mu_{lat}}$$

where μ_{imp} represents scattering due to impurity ions and μ_{lat} represents scattering due to phonons. The scattering of electrons at low temperatures are dominated by impurity atoms, at high temperatures lattice scattering becomes more prominent.

From the above expression of R_{xy}^z it is clear that the magnitude as well as the sign of the Hall coefficient depend on the number of free carriers, their nature and their mobility at the temperature under consideration. In the present case, a very low amount of acceptor impurity is added to pure bismuth so that the Fermi level lies within the overlap region. The density of electrons in L_C is sufficient at low temperature and the mobility of electrons is much greater than that of holes. Then it is possible that the effective contribution of electrons towards the Hall coefficient is greater than that of holes, which makes the term A_1 in the expression of R_{xy}^z negative, resulting in negative Hall coefficient at low magnetic filed strengths.

As the temperature rises, 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, those 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 the same number of holes in L_V. In this way the gains in the concentration of three types of carriers make the Hall coefficient small at higher temperature. In addition the effect of phonon scattering may also be there in the variation of Hall coefficient.

As it is clear from the expression of Hall coefficient, the increase of the applied magnetic field strength decreases the magnitude of Hall coefficient. For higher magnetic filed strength total contribution of two types of holes towards the Hall coefficient prevails over that of the electrons, thereby making it positive at low temperature. The high mobility value of the electron may have an important role for the Hall coefficient to be positive. In this field strength the effect of scattering by lattice vibrations and defect centers which controls the relaxation time and thus mobility of the carriers becomes important in the high temperature range. The concentration of electrons in the L_C band grows faster with temperature than the holes. This scattering mechanism and the sufficient number of free electrons make the Hall coefficient value to vary with temperature towards the small and negative value.

The results here point to the variation of the concentration of three different types of carriers with differences in their masses (mobility) and the scattering mechanism with temperature, which are mainly responsible for the observed unusual n-type behaviour.

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