Thermoelectric and Transport Properties of Semi-conducting $Bi_{88}Sb_{12}$ Alloy

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Abstract

Homogenized sample of $Bi_{88}Sb_{12}$ was prepared by quenching and annealing at 523 K for 200 days. It is an n-type semiconductor, and its properties show different temperature dependences between the low-temperature ($T <$ 70K) and high-temperature ($T >$ 70K) regions. Chemical potential was calculated from the measured carrier concentration, and found to change abruptly at 70 K, increasing rapidly with temperature. This explains the above differences in the two temperature regions in the framework of the Boltzmann theory, indicating $Bi_{88}Sb_{12}$ is a strongly degenerate semiconductor.

Key words: Bismuth-antimony alloy; Semiconductor; Hall effect; Thermoelectric effect

1. Introduction

$Bi_{100-x}Sb_x$ alloy is a direct-gap semiconductor in the composition range of $9< x <15$ [1]. These alloys are expected as the best materials for thermoelectric cooling in the low temperature range [2,3]. However, it is difficult to prepare the $Bi_{100-x}Sb_x$ crystals of high homogeneity because the liquidus and solidus lines are apart from each other in the phase diagram of Bi-Sb system, resulting segregation in the melt-grown crystals [4]. In the present study, semi-conducting $Bi_{88}Sb_{12}$ alloy is prepared by quenching and annealing, in order to obtain the homogeneous sample. The Hall and Seebeck coefficients were measured in the temperature range from 20 to 300K. These thermoelectric and transport properties are discussed on the basis of Boltzmann theory of transport.

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2. Experimental Procedure

The constituent elements, Bi and Sb were weighed to make $Bi_{88}Sb_{12}$ and directly melted in an evacuated quartz ampoule. The ampoule was kept at 1073 K for 4 hrs, and then quenched into ice water. The ingot was annealed at 523K for 200 days in order to diminish the segregation. For this sample, the electrical resistivity ρ, Hall and Seebeck coefficients R_H and α were measured in the temperature range from 20 to 300K.

3. Experimental Results

The sign of Hall coefficient R_H is negative in all temperature range, so we can confirm that majority carrier is electrons. The carrier concentration n increases with temperature, as is generally the case for a typical semiconductor. The Hall mobility $\mu_{\rm H}$ was calculated from $\mu_{\rm H}=R_{\rm H}/\rho$. Each $\log\mu_{\rm H}$ - $\log T$ relationship shows a discontinuous change at about 70K between two linear relationships. The data can be well fitted by using

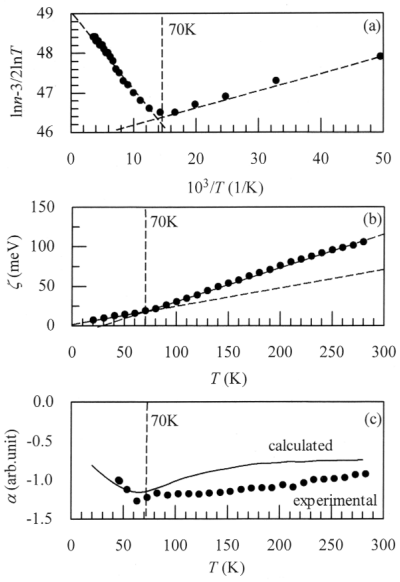

Fig. 1. (a) Plot of ln$n$-3/2ln$T$ against $1/T$. (b) Evaluated chemical potential ζ as a function of T. (c) Temperature dependence of Seebeck coefficient α. Calculated by using ζ (solid line) and experimental value (black circles)

the classical expression of $\mu_{\rm H} \propto T^{s-1}$ for phonon scattering. The scattering factor s can be estimated from the slopes as s=0.38 at lower temperatures, and s=-1.78 at higher temperatures. As we decrease the temperature, the electrical resistivity ρ shows a gradual change down to $T >$ 70K and then abrupt decrease for $T <$70K. The Seebeck coefficient α shows the negative sign in the whole temperature range, and it is consistent with that of the Hall coefficient. The absolute value of α takes a maximum value around 70K. Thus temperature dependences of semiconductive and thermoelectric properties unanimously change near 70K.

4. Discussion

It is remarkable that T = 70K is a special point separating the two temperature ranges. In particular, the Seebeck coefficient behaves quite differently, depending on the ranges. It strongly suggests that the system undergoes a fundamental change at this particular temperature, either in the scattering mechanism or in the electronic structure. We will show that it is the change in the electronic structure which is responsible for the difference between the two temperature regions.

This is not quite visible in the carrier concentration data, but may be elucidated by plotting it against $1/T$, as shown in Fig.1(a).

In this plot the change is seen to be rather abrupt, occurring at $T = 70K$, as though it consists of the two straight-lines. Recalling the classical relation

$$n = \frac{1}{4}\left(\frac{2kT}{\pi\hbar^2}\right)^{\frac{3}{2}} m^{*\frac{3}{2}} e^{\frac{\zeta}{kT}} \qquad (1)$$

between the carrier concentration n and the chemical potential ζ, these linear changes imply that the chemical potential also changes linearly in T in each of the temperature ranges. We have evaluated ζ as a function of T, by setting m^*/m=0.02 and solving (1) for ζ. This is shown in Fig.1(b). The chemical potential indeed increases linearly with T, and changes the rate suddenly at T = 70K. This behaviour is due to the peculiarity of the electronic structure, with a very small band gap and an extraordinary small effective mass of the conduction band. The low density-of-states of the conduction-band causes a rapid increase of ζ on heating, particularly after the extrinsic-to-intrinsic transition. The low transition temperature of $70K$ implies the smallness of the band gap. This consideration is consistent with the study by B. Lenoir et.al [5].

As a tentative analysis, we have applied the Boltzmann theory to the Seebeck coefficient (Fig.1(c)) by using ζ obtained above. Calculated value reproduces the experimental value qualitatively, showing a clear minimum around the same temperature. As a theoretical prediction, we can state that the maximum absolute value of the Seebeck coefficient is associated with the extrinsic-to-intrinsic transition, and the maximum is realized around the transition temperature. The high-performance of the Bi-Sb alloy as a thermoelectric material is a result of the smallness of the conduction-electron effective mass. At room temperature, the value of ζ amounts to as high as 120 meV in the present calculation. This is expected to be one-order of magnitude larger than the band gap. Therefore Bi-Sb alloy serves as a typical example of a strongly degenerate semiconductor, and its transport properties may be understood on the basis of the Boltzmann theory when the degeneracy is fully taken into account.

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