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Abstract. The electrical resistivity, ρ, was measured for the melt of a typical III–V semiconductor system, Ga–Sb, by the direct-current four-probe method. Similarly to the case for solid substitutional alloys, the Nordheim rule almost establishes the concentration dependence of ρ. That is, a rather parabolic form of $\Delta\rho$ was obtained as a function of composition; $\Delta\rho$ is the deviation of the resistivity from the linear law relating the resistivities of the pure components, liquid Ga and liquid Sb. In spite of this rather simple behaviour of the concentration dependence of ρ itself, its temperature coefficient, $d\rho/dT$, shows a clear minimum at the eutectic composition and even a negative temperature coefficient was observed near the eutectic point. This negative $d\rho/dT$ may be the first indication for the existence of particular hidden structure, related to concentration fluctuations, in the liquid near the eutectic point. In addition, this strange behaviour of $d\rho/dT$ was discussed on the basis of the effective-medium theory.

1. Introduction

In most cases the solid semiconductor compounds are composed of elements with different characters, typically expressed as those of III–V and II–VI semiconductor compounds [1]. Therefore the interactions between the two components are very strong and in many cases these compounds show high melting points. On melting, these strong interactions are destroyed and these compounds change from semiconductors into metals from the electronic point of view [2]. However, in the melt of semiconductor materials the strong chemical short-range order can be expected to remain [3]. Therefore it is very interesting to study the melts of these semiconductor compounds from the fundamental point of view. The most direct method for this purpose is probably structural studies based on x-rays and neutrons, such as diffraction experiments including the small-angle scattering experiments, EXAFS and anomalous x-ray scattering studies, etc. However, prior to carrying out these direct structural studies, it is also important to study these liquids with complex structures in detail using conventional laboratory experimental methods, such as measuring the electrical resistivity, ρ, viscosity, η, etc. The purpose of this paper is to report the curious features of ρ—particularly the unusual temperature coefficient of ρ, $d\rho/dT$, for the liquid III–V system, Ga–Sb. The hidden liquid structure is shown to exist in the liquid state near the eutectic composition on the basis of the temperature coefficient of ρ, $d\rho/dT$, though it cannot be detected from the observation of the concentration dependence of ρ alone.

2. Experimental procedure

The electrical resistivity, ρ, was measured by the dc four-probe method during cooling from 1173 K down to the liquidus temperature. The cell design used is shown in figure 1. The cell was made of quartz glass and the tungsten electrodes were inserted into carbon lids. The sheaths for the thermocouples, made of thin quartz tubes, were also inserted in the centre of these lids. The temperature was measured by the alumel–chromel thermocouples, which were inserted into these quarts sheaths. This cell was placed in a Mo–Si furnace, which has the function of mixing the sample and introducing it into the capillary part. The concentration of the sample was determined by weighing. The purity of the metals used was 6N, both for the Ga and for the Sb.
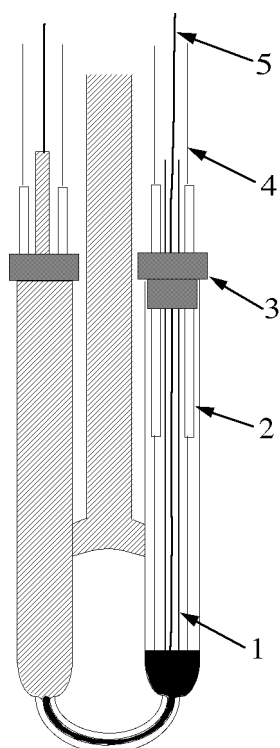

Figure 1. The design of the cell used. 1: quartz sheath; 2: insulating tube; 3: graphite plug; 4: tungsten electrodes; 5: alumel–chromel thermocouples with a thin stainless steel sheath.

3. Results

In figure 2 we show the temperature dependence of the electrical resistivity, ρ, of the liquid Ga–Sb system. The concentration dependence of ρ and its temperature coefficient, $d\rho/dT$, are shown in figures 3 and 4 respectively. The reproducibility of the measurements of ρ is within $\pm0.5\%$ and that of $d\rho/dT$ is within ±0.0005 $\mu\Omega$ cm K^{-1}.

4. Discussion and conclusions

The concentration dependence of the electrical resistivity, ρ, in the liquid state shows a rather monotonic behaviour, as shown in figure 3. In a previous study the maximum of ρ in the
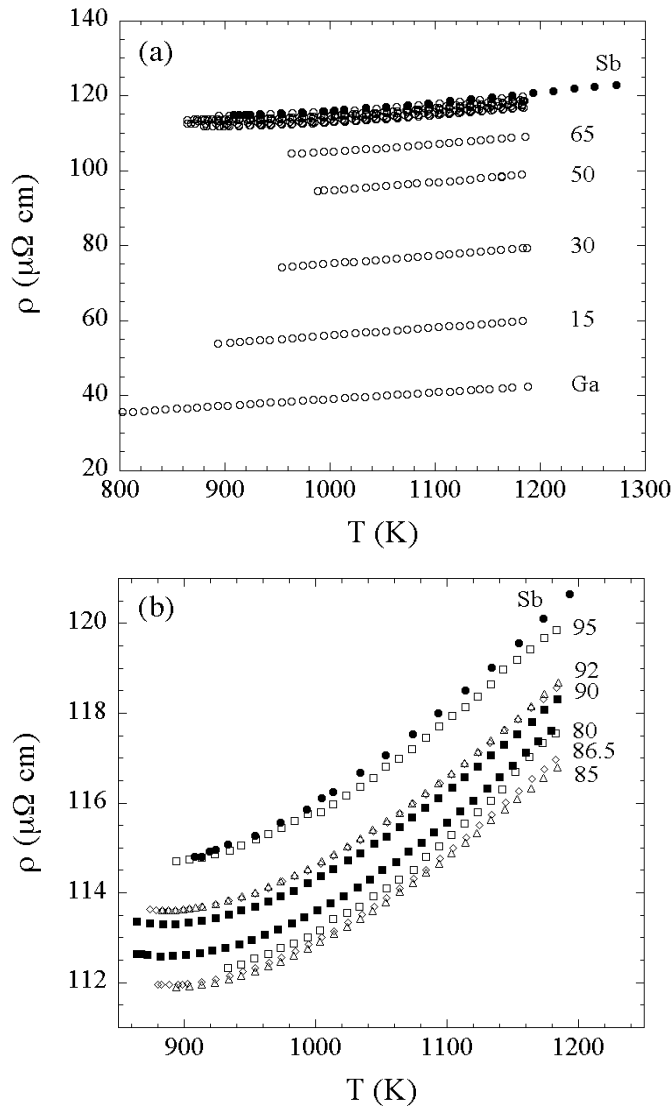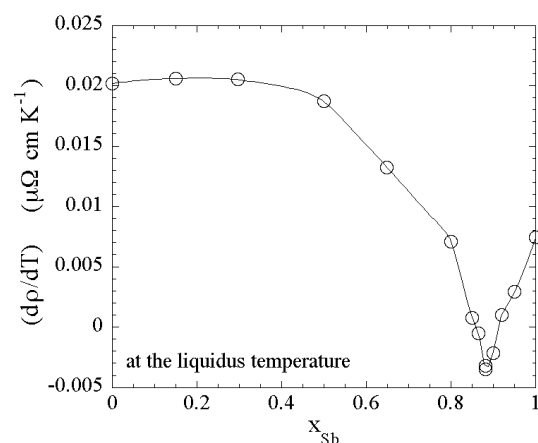
Figure 2. The temperature dependence of the electrical resistivity of the liquid Ga–Sb system (a) and a magnified view for samples near the eutectic composition (b). ■: eutectic compositions (88.2 at.% Sb).

liquid state was reported by Glazov *et al* [2] at the 1:1 composition, GaSb. In this study no such anomalous behaviours were observed. In addition, as shown in figure 5, a rather simple parabolic relation was found for the concentration dependence of the deviation of ρ from the linear law, which is defined as $\Delta\rho$; $\Delta\rho = \rho - [x_{Sb}\rho_{Sb} + (1 - x_{Sb})\rho_{Ga}]$; x_{Sb}: the atomic fraction of Sb; ρ_i: the resistivity in the liquid state of component i. This parabolic relation is known as the Nordheim rule, which is strictly valid for the substitutional solid alloys [4], such as the solid Au–Cu system. Therefore, the concurrence with the Nordheim rule for liquid Ga–Sb alloys in figure 5 indicates that the structure of liquid Ga–Sb seems to be rather simple and not so far from the substitutional distribution between Ga and Sb atoms.
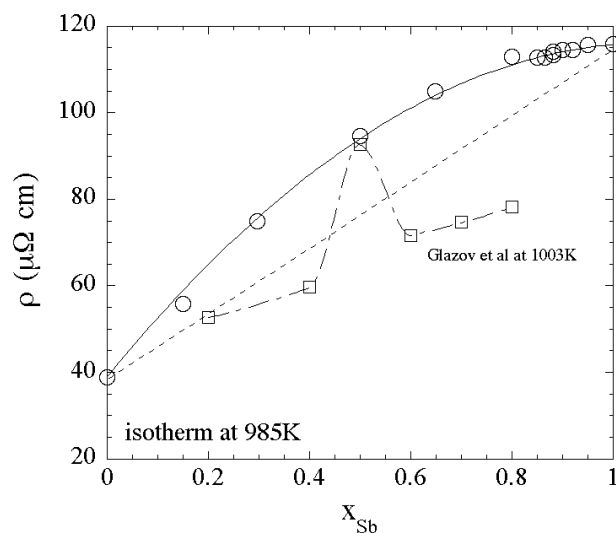
Figure 3. The concentration dependence of the electrical resistivity for the liquid Ga–Sb system at 985 K and previously obtained 1003 K data from Glazov *et al* [2]. $\bigcirc$: present data; $\square$: data from Glazov *et al* [2]; $---$: the linear law.

Figure 4. The concentration dependence of the temperature coefficient of the electrical resistivity for the liquid Ga–Sb system at the liquidus temperature.

However, a quite strange behaviour is seen in the concentration dependence of the temperature coefficient of the electrical resistivity, $d\rho/dT$, as shown in figure 4. This figure was drawn at the liquidus temperature and an essentially similar tendency (a minimum of $d\rho/dT$ around the eutectic composition, though its tendency is weak) was observed for the isotherm at 985 K, which corresponds to the highest melting temperature among those of the solid-phase, intermetallic GaSb compounds in the Ga–Sb system. $d\rho/dT$ at the liquidus temperature shows a strong minimum phenomenon at 88.2 at.% Sb though no anomalous behaviour is observed at the 1:1 composition, GaSb. In this experiment we planned to measure the temperature of the sample as accurately as possible by inserting two thermocouples into the liquid alloy sample in two quartz sheaths, as shown in figure 1. In this way, the accuracy of
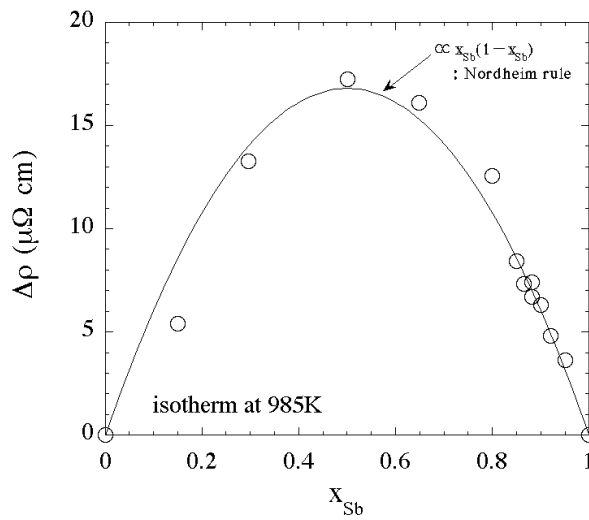
Figure 5. The deviation of the electrical resistivity from the linear law at 985 K. ——: the Nordheim rule.

the measurements of $d\rho/dT$ may be kept very good in the present experiment. In view of the anomalous behaviour of $d\rho/dT$ in figure 4, an anomalous structure is expected at the eutectic composition (88.2 at.% Sb) rather than the 1:1 composition of the intermetallic compound, GaSb. In addition it is to be noted that even a negative $d\rho/dT$ can be seen near the eutectic composition (from 86.5 to 90 at.% Sb), as shown in figure 4. In the inset in figure 6 we show a
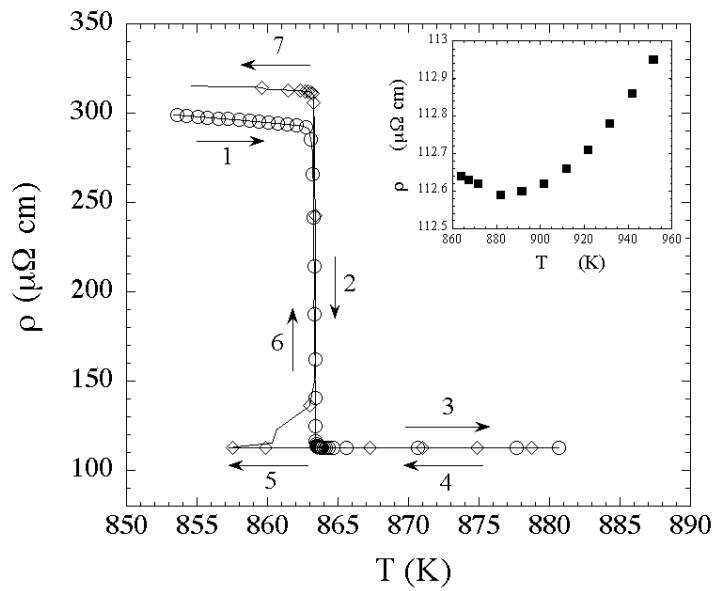

Figure 6. A magnified view of the temperature dependence of ρ at the eutectic composition (inset) and the electrical resistivity in the heating-and-cooling cycle for the eutectic sample after solidification. Numbers indicate the order of the measurements in the cycle.

magnified view of ρ for the Ga–Sb alloy with the eutectic composition. The negative $d\rho/dT$ can be observed below 880 K. In this figure the electrical resistivity, ρ, in heating-and-cooling cycles, is also shown for the sample after solidification. From this measurement the eutectic temperature was determined to be 863.2 K, which is close to the eutectic temperature, 862.3 K, found in [5]. Thus a negative temperature coefficient of ρ over a temperature range of 17 K (from 880 K to 863 K) was certainly found in the equilibrium homogeneous liquid phase.

To date, the negative temperature coefficient of ρ has been found for liquid alloys for two cases. One case is that of liquid alloys with large electrical resistivities, such as liquid Mg–Bi alloys [6]. In this case, the values of ρ exceed the criterion of Mott [7] for the metal–semiconductor transition—that is, $300\ \Omega^{-1}\ cm^{-1}$ for the electrical conductivity or $3000\ \mu\Omega\ cm$ for the electrical resistivity. The second case is that of liquid alloys with comparably small electrical resistivities whose ratio of the number of valence electrons to that of atoms is near 2 [8, 9]. The first case does not correspond to the present situation, judging from the small value of ρ. The second case is also not the present situation, because of the combination of trivalent and pentavalent atoms with rather low electrical resistivities for liquid Ga–Sb alloys. Thus, anomalous negative behaviours of $d\rho/dT$ in the temperature range of 17 K above the eutectic temperature, found in this study, cannot be explained by existing theories conventionally employed to date, as described above.

Here it is very instructive for the understanding of the role of concentration fluctuations in the resistivity of liquid metals to note the previous works of Adams [10] and Schürmann and Parks [11, 12]. In these studies, anomalous behaviours of ρ and $d\rho/dT$ for some liquid alloys with two-liquid-phase separation were observed with the approach to the critical point for liquid Hg–Ga [10], Bi–Ga [10,11], and Li–Na [11] systems. It is concluded, particularly in the paper of Schürmann and Parks [11], that these anomalous behaviours of ρ and $d\rho/dT$ above the critical temperature derive from the growth of concentration fluctuations with the approach to the critical point for liquid Bi–Ga and Li–Na, though attention should be paid to the false anomaly due to the effect of rapid gravitational separation of two liquid phases [12]. In [11], $d\rho/dT$ seems to be more sensitive to concentration fluctuations than ρ itself. The existences of such anomalies derived from concentration fluctuations have been revealed for liquid alloys with critical mixing by means of measurements of the heat capacity [13, 14], ultrasonic absorption [15], viscosity [16], thermoelectric power [17], and small-angle scattering of neutrons or x-rays [18–22]. Recently, experimental studies of ρ for some liquid alloys with two-liquid-phase separation were performed in detail both under gravity and under microgravity, and the temperature coefficient, $d\rho/dT$, is found to be a good indicator of concentration fluctuations in the homogeneous liquid phase [23, 24].

Therefore this negative temperature coefficient, or the minimum of the temperature coefficient in liquids near the eutectic point, shown in figures 4 and 6, may be derived from concentration fluctuations, which may be related to the particular features of liquids near the eutectic point for the Ga–Sb system. At this eutectic composition in the solid state, two solid phases of the intermetallic compound, GaSb, and semimetal, Sb, coexist. Thus it is thought that, even in the liquid state, near this eutectic composition this particular feature can be expected to be present, relating to the phase separation in the solid state. That is, there may be concentration fluctuations, in which Sb-like (domain 1) and GaSb-like (domain 2) domains may be present in the homogeneous liquid domains (domain 3) near the eutectic point.

The effect of concentration fluctuation on the electrical resistivity or electrical conductivity can be simply considered within the mean-field theory; the relevant expression is given in the textbook of Cusack [25] for a medium with two kinds of randomly distributed conducting domain. Recently, Masaki *et al* [26] have extended this theory to the case of a medium with three kinds of randomly distributed conducting domain; this extended theory successfully

applied to the problem of two-liquid-phase separations. The explicit form is as follows:

$$\phi_1 \frac{(\sigma_1 - \sigma_m)}{(\sigma_1 + 2\sigma_m)} + \phi_2 \frac{(\sigma_2 - \sigma_m)}{(\sigma_2 + 2\sigma_m)} + \phi_3 \frac{(\sigma_3 - \sigma_m)}{(\sigma_3 + 2\sigma_m)} = 0. \tag{1}$$

In this equation, σ_1, σ_2, and σ_3 are the electrical conductivities of domains 1, 2, and 3; σ_m is the electrical conductivity of the medium as a whole with three kinds of randomly distributed conducting domain; ϕ_i is the volume fraction of domain i. It can be assumed that domain 1 and domain 2, respectively, correspond to the Sb domain and the GaSb domain. Domain 3 corresponds to the homogeneous domain, in which no concentration fluctuations can be observed. Domain 2 is expected to become semiconducting. On the other hand, the electrical resistivities of domains 1 (Sb) and 3 (the homogeneous phase) can be considered to be metallic. Thus, it is sufficient for qualitative discussions of the behaviour of the resistivity to consider the conditions $\sigma_m \simeq \sigma_1$, $\sigma_m \gg \sigma_2$, and $\sigma_m \simeq \sigma_3$. Inserting these conditions in equation (1), the following expressions can be obtained easily:

$$\sigma_m = \sigma_3 \phi_3 \tag{2}$$

or

$$\rho_m = \rho_3 / \phi_3. \tag{3}$$

In equations (2) and (3), σ_m (ρ_m) corresponds to the electrical conductivity (resistivity) of the medium as a whole with three kinds of randomly distributed conducting domain; σ_3 (ρ_3) corresponds to that of the homogeneous domain. With the approach to the eutectic point in the homogeneous liquid in the cooling process, the degree of concentration fluctuations becomes larger. Thus, in this process, ϕ_1 and ϕ_2 increase slightly and ϕ_3 decreases slightly, although ϕ_3 remains almost 1. Therefore ρ_m is larger than ρ_3 ($\rho_m > \rho_3$)—but only slightly, because the value of ϕ_3 is only slightly smaller than 1. In other words, on cooling, the degree of decrease of the resistivity (typical metallic behaviour) is suppressed slightly by the slight decrease of ϕ_3. This brings about the decrease of the temperature coefficient of the resistivity. The above discussions may be clarified if the temperature coefficient of ρ_m, $d\rho_m/dT$, is written out explicitly by using equation (3):

$$\frac{d\rho_m}{dT} = \frac{1}{\phi_3} \frac{d\rho_3}{dT} - \frac{\rho_m}{\phi_3^2} \frac{d\phi_3}{dT}. \tag{4}$$

That is,

$$\frac{d\rho_m}{dT} \simeq \frac{d\rho_3}{dT} - \rho_m \frac{d\phi_3}{dT}. \tag{5}$$

The first positive term in equation (5) is suppressed by the second term and this may be the cause of the decrease of $d\rho/dT$ near the eutectic point, as shown in figure 4. The negative $d\rho_m/dT$ may appear under the condition $d\phi_3/dT > (d\rho_3/dT)/\rho_m$. The magnitude of $(d\rho_3/dT)/\rho_m$ can be estimated to be of order 2×10^{-4} K^{-1}, for example, from the values estimated at $x_{Sb} = 0.5$ from figures 3 and 4. Therefore, without a large variation of the value of ρ_m itself, negative temperature coefficients may be possible under the condition (for example) $d\phi_3/dT > 2 \times 10^{-4}$ K^{-1} in the narrow temperature range near the eutectic point.

The value of ρ for liquid Ga–Sb is not so large and the Faber–Ziman theory based on the nearly-free-electron model may be also applicable. However, in view of the large degree of concentration fluctuation, at least many kinds of correlation function are required for the analysis of electron transport based on the Faber–Ziman theory even for the same atomic pairs, depending on the domains. Such analyses seem likely to be much too complicated, and in this study the mean-field theory was adopted to stress the role of concentration fluctuations simply. In principle, this theory is valid for macroscopic and mesoscopic systems. However, the validity

of this theory for the present case may be slightly supported by the rather small value of the mean free path of the conduction electrons, λ_F—comparable to the interatomic distance d (the estimated value of $\lambda_F/d = 1.2$ for the melt of eutectic composition for Ga–Sb). Domains of concentration fluctuations with a size of a few tens of ångströms (see for example [20]) may be rather macroscopic. This analysis may be much too simplified and further studies must be done to establish the origin of the negative $\mathrm{d}\rho/\mathrm{d}T$.

Probably for the first time, in this paper it was revealed that particular liquid structures or concentration fluctuations are hidden in the liquid state near the eutectic point, for the liquid state of the III–V semiconductor Ga–Sb system. We are now obtaining similar results for the liquid In–Sb system. These results will be published in the near future. In the next stage, it is very important to describe this particular structure of liquids in a more vivid manner. For this purpose, structural study, which must be sensitive to the intermediate order, may be important.

Acknowledgments

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