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Abstract

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ON THE BEHAVIOR OF ALUMINUM, GALLIUM, AND INDIUM ANTIMONIDES IN THE LIQUID STATE

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The aim of the present work was to study the temperature dependence of the magnetic susceptibility of aluminum, gallium, and indium antimonides in the liquid state and to compare the data obtained with some of their thermodynamic and kinetic properties. Investigation of these compounds in the molten state is of practical importance, since the main stages in the technology of obtaining them for use as semiconductors (purification by crystallization methods and the production of single crystals) are associated with the liquid state. The study of the properties of melts of compounds is also of interest for the theory of the liquid state, since up to the present time the question cannot be considered clarified as to what, structurally, melts of intermetallic compounds represent and by what the arrangement of atoms in the liquid state is determined: by the structure of the pure components or by the structure of the solid alloy (⁀1).

Certain conclusions about the structure of a liquid can be drawn on the basis of comparing various physicochemical properties that are related to one another, since all of them, in the final analysis, depend on one fundamental cause–the state of the electrons in the melt. In this connection, it is meaningful to establish relationships among different properties of a liquid.

Magnetic susceptibility is a very sensitive characteristic, responding to the slightest changes in the state of the electrons (or even of a fraction of the total number of electrons) in the melt, and therefore in the present case it may prove especially useful.

Investigation of magnetic susceptibility as a function of composition in the liquid state in systems with intermetallic compounds (⁀2) made it possible to establish the fact of chemical interaction between the components in the liquid state (the ordinate of the chemical compound corresponds to a clearly expressed minimum).

For the compounds considered in the present work, the temperature dependence of electrical conductivity, density, and viscosity had previously been studied ([3],4). It was also shown (⁀4) that the liquidus lines in the aluminum–antimony,

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gallium–antimony, and indium–antimony systems have a singular maximum, which indicates the stability of these compounds on melting. The curves of the temperature dependence of their electrical conductivity and density in the liquid state have a smooth course (^3). In the study of the temperature dependence of viscosity, a deviation from the regular course of the curves was found at a certain superheating, which was associated with the beginning of noticeable dissociation of the compounds in the liquid state. In addition, in studying the dependence of the free energy of activation of viscous flow of melts of aluminum, gallium, and indium antimonides (^5), an anomalous, in comparison with typical metals, course of it in the precrystallization···

zation period, which was associated with definite changes in the structure of short-range order in these melts.

All the indicated changes ([4],5), evidently, are connected with corresponding substantial changes in the state of the electrons in melts of aluminum, gallium, and indium antimonides. In this connection it was decided to investigate in detail the temperature dependence of their magnetic susceptibility in the liquid state.

As starting materials we used compounds AlSb, GaSb, and InSb that had been synthesized in advance and purified by the methods of zone recrystallization and pulling. Samples of gallium and indium antimonides were placed in evacuated quartz ampoules. The compound AlSb was placed in a corundum crucible, which, in turn, was placed in an evacuated quartz jacket.

Fig. 1. Dependence of magnetic susceptibility (in relative units) on temperature for the compounds AlSb, GaSb, InSb

The magnetic susceptibility was determined by the Faraday method on an apparatus described in detail in (^6). The magnetic-susceptibility values were taken as the averages of three measurements. The mean error in weighing was ±0.2 mg. The results of the measurements are presented in Fig. 1.

As follows from the graphs shown, the temperature dependences of the magnetic susceptibility of the compounds AlSb, GaSb, and InSb in the liquid state are similar in form. This indicates that, upon heating all three compounds, identical or very similar processes occur in them.

On the curves of the dependence of magnetic susceptibility on temperature one can distinguish four regions. At first, when the melts are heated from the melting temperature, the magnetic susceptibility increases and reaches a maximum, and then decreases. With further heating the magnetic susceptibility again increases, again reaches a maximum, and again decreases.

When the data obtained are compared with the results of studies of the temperature dependence of viscosity (^4) and of the free activation energy of viscous flow (^5) of aluminum, gallium, and indium antimonides, the following points attract attention:

1) The first maximum (counting from t_m) on the curves of the dependence of magnetic susceptibility on temperature for these substances coincides fairly accurately with the minimum on the curve of the temperature dependence of the free activation energy of viscous flow, the presence of which was associated with a rearrangement of the short-range-order structure, accompanied by a corresponding change in the number of atoms in the first coordination sphere (^5).

2) The minimum on the magnetic-susceptibility curve upon further heating of the melts of the compounds corresponds approximately to the same temperatures at which deviations from the regular course of the temperature-dependence curves of viscosity are observed. These deviations, apparently, are connected with the onset of noticeable dissociation of the chemical compounds AlSb, GaSb, and InSb in the liquid state (^4).

Thus, relying on the results obtained and on the results of earlier work, one may present the following probable picture of the behavior of the compounds under consideration in the liquid state (^4).

At the melting temperature, the melts of the compounds have approximately the same short-range-order structure as in the solid state. As the temperature increases, the coordination number increases (this corresponds to an increase in the magnetic susceptibility of the melts of the compounds), approaching close packing at a certain temperature. An analogous conclusion concerning changes in the liquid state in elements that possess a loose structure in the solid state was made in work ([7]) on the basis of electron-diffraction studies of liquid films of tin and bismuth. The temperature at which relatively close packing is attained in the liquid corresponds to the first maximum on the curves of the temperature dependence of magnetic susceptibility and to the minimum on the curves of the temperature dependence of the free energy of activation of viscous flow ([5]).

Upon further heating up to a certain limit, no changes occur in the melts of the compounds AlSb, GaSb, and InSb except those that accompany the heating of any liquid (weakening of intermolecular interaction forces, increase in intermolecular distances, increase in the number of vacancies, etc.). In this temperature interval the chemical compound is relatively stable in the liquid state. This is also evidenced by the presence of singular extrema (a minimum of electrical conductivity and a maximum of viscosity) on the composition–property isotherms corresponding to this temperature interval. In this region the properties change monotonically: the magnetic susceptibility and viscosity decrease smoothly, while the free energy of activation of viscous flow increases linearly.

Upon reaching a certain temperature, which is determined by the individual properties of the compound, the latter begins to dissociate intensively (these temperatures correspond to the minimum on the curves of the temperature dependence of magnetic susceptibility and to deviations from regular behavior on the curves of the temperature dependence of their viscosity ([4])).

With further heating, the degree of dissociation increases and, in connection with this, the magnetic susceptibility rises. Upon reaching certain significant degrees of dissociation, the temperature factor proves to be predominant, as a result of which the magnetic susceptibility again begins to fall.

Thus, on the basis of the study and comparison of various physicochemical properties of melts of the antimonides of aluminum, gallium, and indium, it is possible to form an idea of their behavior in the liquid state. The information obtained on the behavior of these compounds in the molten state should be taken into account in the synthesis and purification of them by crystallization methods, as well as in obtaining single crystals with a more perfect structure.

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Note: Figure translations are in progress. See original paper for figures.