Nuclear Magnetic Resonance Studies of Liquid Semiconducting Sb-Te Alloys

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Nuclear magnetic resonance studies of ^{123}Sb and ^{121}Sb in the Sb_xTe_{1-x} liquid alloy system are described. Interest is focussed on the concentration dependence of the Knight shift and the NMR linewidth. Measurements of the Knight shift and linewidth have been carried out over the entire concentration range at elevated temperatures (900 – 1100) K. Knight shifts of ^{123}Sb and ^{121}Sb, measured to high precision, show hyperfine structure anomaly. Both, Knight shift and linewidth show strong dependence on the alloy concentration and extreme behavior at the concentrations 40 at.% Sb and 50 at.% Sb, respectively. The experimental results are discussed in terms of modes concerning the electronic structure of liquid semiconductors.

1. Introduction

The electronic structure of liquid semiconductors changes significantly with composition. Systematic investigations in this field can contribute to our understanding of the relation between the atomic and electronic structure of matter. Additionally, insight into the physics of liquid semiconductors will be useful for the understanding of the physics of amorphous solid semiconductors. Elaborated theories in the field of both liquid and amorphous solid semiconductors are in a rather early stage. Therefore, at this stage experimental results are of particular importance. We present in this paper Knight shift measurements of ^{123}Sb over the entire concentration range at high temperatures. In a good approximation, for liquid semiconductors proportionality between Knight shift K and density of states at the Fermi energy $N(E_F)$ has been found [1]. Thus, changes in K with a parameter (e.g. concentration) are directly connected with changes in $N(E_F)$.

2. Experimental

The measurements were carried out with a cw-NMR spectrometer operating in the range (25 – 55) MHz. The external magnetic field, which was calibrated with deuterium NMR, has been generated by a superconducting solenoid [2]. The high temperature furnace was constructed using a Pt-10% Rh wire bifilar heating element. In order to avoid disturbing magnetic fields at the position of the NMR sample we constructed a furnace using materials which are characterized by a magnetization with weak temperature dependence [3]. The temperature was measured to an accuracy of ± 5 °C with a Pt vs. Pt-10% Rh thermocouple. The samples were made from 99.999% purity Sb and Te (supplied by Ventron Corporation). The alloy components, in an Al_2O_3 crucible, were melted together in a quartz ampulla under a vacuum of 10^{-5} Torr. The material was made homogeneous by shaking and leaving it for 4 days at temperatures higher than the melting point of the alloy under preparation. The melt was sealed in the quartz ampulla before being water quenched. For the NMR samples the starting material was crushed and sieved to give particles with a diameter less than 50 μm. The sample obtained was annealed and degassed for 60 h in a quartz tube before the measurement.

3. Results

3.1 Pure Sb metal

The Knight shift K of both isotopes of ^{121}Sb and ^{123}Sb has been measured in pure liquid antimony at the melting point. $HSbF_6$ served as a reference compound. The measured shifts were found to be

$$K(^{121}\mathrm{Sb}) = (0.7035 \pm 0.0008)\,\% \,,$$

$$K(^{123}\mathrm{Sb}) = (0.7053 \pm 0.0008)\,\% \,.$$

It has to be emphasized that although the isotope ^{121}Sb possesses a larger magnetic moment than

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^{123}Sb, it shows a smaller Knight shift. Our experimental results show that $K(^{121}\mathrm{Sb})$ and $K(^{123}\mathrm{Sb})$ have clearly different values in liquid Sb. Earlier measurements of $K(^{121}\mathrm{Sb})$ and $K(^{123}\mathrm{Sb})$ [4] in liquid Sb did not show any difference between the shifts:

$$K(^{121}\mathrm{Sb}) = K(^{123}\mathrm{Sb}) = (0.709 \pm 0.010)\ \% .$$

But a hyperfine structure anomaly for ^{121}Sb and ^{123}Sb has been reported in [5] for the liquid GaSb system, and the following values were given:

$$K(^{121}\mathrm{Sb}) = (0.6696(3)\ \% ,$$

$$K(^{123}\mathrm{Sb}) = (0.6720(3)\ \% .$$

For the NMR linewidths ΔB of ^{121}Sb and ^{123}Sb in liquid pure Sb at the melting point we found:

$$\Delta B(^{121}\mathrm{Sb}) = (2.35 \pm 13)\ \mathrm{G} ,$$

$$\Delta B(^{123}\mathrm{Sb}) = (1.89 \pm 13)\ \mathrm{G} .$$

3.2 Alloys

Our experimental results for $K(^{123}\mathrm{Sb})$ as a function of concentration in the liquid Sb-Te system for several temperatures are plotted in Figure 1. Pronounced minima of the isotherms appear at the stoichiometric composition Sb_2Te_3. These are the first Knight shift results in liquid Sb-Te over the entire concentration range. Previous results for concentrations up to 23 at.% Te [6] and for 60 at.% Te [7] are in good agreement with our results.

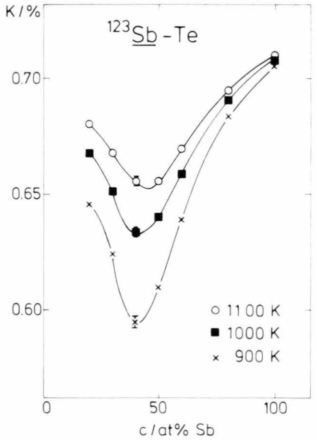

Fig. 1. The ^{123}Sb Knight shift K in liquid Sb-Te system as a function of concentration with the temperature as a parameter.

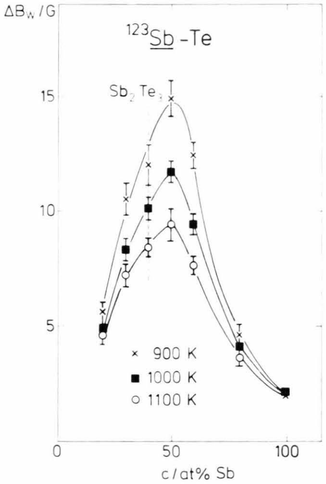

Fig. 2. The NMR linewidth of ^{123}Sb in liquid Sb-Te systems as a function of concentration with the temperature as a parameter.

Figure 2 shows the concentration dependence of the NMR linewidth $\Delta B(^{123}\mathrm{Sb})$ in liquid Sb-Te for different temperatures. A maximum appears for all isotherms at 50 at.% Te. The NMR linewidths of ^{121}Sb and ^{123}Sb in the liquid Sb_2Te_3 compound at the melting point have been found to be

$$\Delta B(^{121}\mathrm{Sb}) = (10.3 \pm 0.7)\ \mathrm{G} ,$$

$$\Delta B(^{123}\mathrm{Sb}) = (12.1 \pm 0.9)\ \mathrm{G} .$$

Thus we found that $\Delta B(^{121}\mathrm{Sb})$ is larger than $\Delta B(^{123}\mathrm{Sb})$ in the pure liquid Sb, whereas in the liquid Sb_2Te_3 compound the opposite is the case: $\Delta B(^{121}\mathrm{Sb})$ is smaller than $\Delta B(^{123}\mathrm{Sb})$.

4. Discussion

4.1. Pure Sb metal

According to our experimental results $K(^{121}\mathrm{Sb})$ is smaller than $K(^{132}\mathrm{Sb})$ in liquid pure antimony. There are different reasons which may be responsible for this isotope effect, e.g.the different nuclear magnetization distributions, so that the interaction with s-like electrons (non-zero probability density at the nucleus) has an isotope-specific character. This effect is expected to be largest for heavy nuclei. There are only few reports referring to the isotope effect on the Knight shift [5], and we need more systematic experimental studies in connection with this matter.

4.2. Alloys

The main contribution to the Knight shift in normal metals and their alloys is assumed to be due to the hyperfine field of the polarized conduction electrons, which interact with the nucleus via the Fermi contact mechanism. This contribution is given by

$$K = \frac{8\pi}{3}\chi_{\mathrm{p}}\Omega\langle|\Psi(0)|^2\rangle_{E_{\mathrm{F}}}, \qquad (1)$$

where χ_{p} is the electronic spin susceptibility per unit volume, Ω the atomic volume, and $\langle|\Psi(0)|^2\rangle_{E_{\mathrm{F}}}$ the average probability density at the nucleus of electrons at the Fermi surface [8]. Other contributions to the Knight shift such as diamagnetic and orbital ones are existent, but for the most liquid simple metal systems they are considerably smaller than the Fermi contact contribution [9], [10], [11], [12]. An additional contribution to K is due to the polarization of the ionic core s-states by P-electrons. This latter contribution is known as core polarization, and for liquid simple metals is assumed to amount to less than 20% of the Fermi contact contribution [12]. Assuming that the Fermi contact term give the main contribution to K and neglecting the other contributions, a change in K with a parameter, for example concentration, reflects change in either or both of χ_{p} and $\Omega\langle|\Psi(0)|^2\rangle_{E_{\mathrm{F}}}$ in (1). Measurements of electrical conductivity and magnetic susceptibility as functions of the concentration in liquid Sb-Te show that a considerable change of the density of states at E_{F} takes place wih change of the concentration [13], [14].

The interpretation of our results is based on the well known assumption that in liquid Sb-Te the constituents form compounds [13]. This synthesis involves particularly the binding of components in their stoichiometric ratios, in the present case Sb_2Te_3. This assumption is in agreement with experimental results concerning electrical conductivity [13], magnetic susceptibility [14], viscosity [13] and other quantities of liquid Sb-Te, which all show an extreme behavior at the concentration corresponding to the stoichiometric composition. Now if the atoms in the liquid system are forming compounds, a reduction of the density of states $N(E)$ will correspond to this process. This is what Mott's pseudogap model describes. But a pseudogap of $N(E)$ at the Fermi energy E_{F} will involve a reduction of χ_{p} in (1) and this consequently a reduction of K. If $N(E_{\mathrm{F}})$ is proportional to χ_{p} and χ_{p} proportional to K, a minimum of $N(E)$ at E_{F} should be expresed by the Knight shift, too. Figure 1 shows that $K(^{123}\mathrm{Sb})$, as a function of the concentration c, has a minimum at $c = 40$ at.% Sb. Thus, Mott's pseudogap model allows a qualitative explanation of our experimental results.

As Fig. 1 shows, the Knight shift K increases with increasing temperature and the minima become less pronounced. This can be qualitatively described with the assumption that with increase in temperature more molecular associations or clusters dissociate. Therefore, the system becomes more "metallic" and the Knight shift increases, too. Electrical conductivity measurements [13] support this assumption. It has been found that the conductivity, which has a minimum value for concentration corresponding to the molecular association Sb_2Te_3, increases considerably with increasing temperature. A comparison of several properties of the liquid Sb-Te system, such as Knight shift, magnetic susceptibility and electrical conductivity, with the corresponding properties of liquid Bi_2Te_3 [15], In_2Te_3 and Ga_2Te_3 [7], [16], shows that liquid Sb_2Te_3 has, like liquid Bi_2Te_3, a rather "semimetallic" character. This is a striking difference to the typical liquid semiconductor systems In_2Te_3 and Ga_2Te_3.

As can be seen in Fig. 2, the NMR linewidth $\Delta B(^{123}\mathrm{Sb})$ in liquid Sb-Te, as a function of concentration, does not show a maximum at 40 at.% Sb (stoichiometric composition), but at 50 at.% Sb. We believe that in liquid Sb-Te the molecular association Sb_2Te_3 is not the only one, but that the association Sb-Te, perhaps with a shorter lifetime, can occur, too. The existence of such associations is connected with stronger interactions between electrons and nucleus. Consequently, stronger dynamic processes occur, which cause enhanced relaxation of magnetic and quadrupolar origin and, therefore; a large linewidth at these critical concentration points. According to the experimental results of relaxation times T_1 and T_2 in liquid Sb_2Te_3 [7], the quadrupolar relaxation relaxation rate decreases with increasing temperature, whereas the magnetic relaxation rate remains almost constant. This means, that the linewidth has to decrease with increasing temperature, and this is what our experimental results show in Figure 2. Measurements of the relaxation times T_1 and T_2 with the pulsed NMR technique over the entire concentration range will give the possibility for a detailed analysis concerning the mechanisms responsible for the NMR linewidth.

Acknowledgement

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