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NMR investigation of rapid structural changes and non-metal-to-metal transition in the molten eutectic Ge–Te alloy

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Abstract

Resonance shift, K^{125}, spin-lattice relaxation time, T_1 and spin–spin relaxation time, T_2 for ^{125}Te nuclei in molten $Ge_{15}Te_{85}$ and Te in deeply under-cooled state have been measured as a function of temperature. The temperature dependence of K^{125} is compared with that of the extent of structural change, C, and it is shown that the rapid increase of K^{125} with increasing temperature can be attributed to an increase of the density of states at the Fermi level proportional to the extent of structural change. At high temperatures, the dependences on the temperature of K^{125} and T_1 conform to the Korringa relation with an enhancement factor or the relaxation mechanism expected metallic nature. At low temperatures, in contrast, the Redfield theory assuming localized spins of which the density is proportional to C can explain the overall temperature dependences of T_1 and T_2. These results provide the first clear evidence for a crossover transition from extended to localized states in the electron system accompanying the rapid structural changes.

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1. Introduction

Ge–Te alloys around the eutectic Ge–Te composition (~15 at.% Ge) show the water-like density anomaly in a narrow temperature range above the eutectic temperature, 648 K [1]. The amount of volume contraction is as large as 7% in the temperature interval of 40°. This structural change is characterized by a strongly peaked extremum in the specific heat, isothermal compressibility and thermal expansion coefficient as a function of temperature [2]. The positions of their extrema for molten $Ge_{15}Te_{85}$ appear around $T = 629$ K and the full width of the half maximum (FWHM) of the peak of the specific heat is about 70°. In this temperature interval the structure of molten $Ge_{15}Te_{85}$ changes very rapidly with changing temperature, which is referred to as a crossover structural transition and its transition temperature or the peak position of the specific heat is denoted by T^* in the following. At temperatures above or below $T^* \pm 40°$, for example, molten $Ge_{15}Te_{85}$ is almost in a high or low temperature form, respectively. The thermodynamic indication of structural changes was preceded by X-ray and neutron diffraction experiments which showed that a small but well-defined pre-peak in the interference function, $S(Q)$, very quickly weakens at temperatures above T^* [3]. A similar but slightly broader crossover structural transition occurs in deeply supercooled molten Te [4], of which the T^* and FWHM are about 623 K and 120°, respectively.

A non-metal-to-metal transition accompanying the crossover structural transition in molten $Ge_{15}Te_{85}$ was

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inferred from a very rapid increase in paramagnetic component of the magnetic susceptibility in a narrower temperature interval as compared with the molten Te case [5]. More direct indication for the non-metal-to-metal transition was obtained by electrical transport measurements [6]. The electrical conductivity increases by a factor three in the same temperature interval. Of significant interest is that the apparent activation energy of the electrical conductivity defined by $E_\sigma = RT^2\partial \ln\sigma/\partial T$ as a function of temperature has a sharp peak around 663 K definitely below T^*. The maximum of E_σ reaches as large as twice the value for $Se_{30}Te_{70}$, for example. From these results it has been suggested that a localized to extended state transition in the electron system occurs at temperatures slightly below T^*.

Warren and subsequently by Dupree et al. have shown that NMR measurements provide invaluable microscopic information on the localized to extended state transition in the liquid semiconductors in terms of the Knight shift and nuclear relaxation times measurements [7,8]. They have demonstrated that a tendency toward the localized state is visualized by the enhancement of the magnetic spin-lattice relaxation rate over the Korringa rate. A subsequent theoretical study has support the idea of the relaxation enhancement [9]. In this work the non-metal-to-metal transition in molten $Ge_{15}Te_{85}$ and Te was investigated by NMR, which includes the resonance shift (K^{125}), spin-lattice relaxation time (T_1) and spin–spin relaxation time (T_2) measurements of ^{125}Te nuclei mainly in the temperature range of structural transition.

2. Experimental details

$Ge_{15}Te_{85}$ alloy was made by direct alloying of Ge and Te pieces in an evacuating fused silica ampoule with inner diameter of about 6 mm. After keeping it at 1273 K for an hour, the ampoule was quenched in water to obtain a uniform glassy specimen. The electrical conductivity of the present specimens is not low enough for radiofrequency penetration of bulk pieces, so that it was necessary to disperse specimens and separate the droplets with approximately equal amount of SiO_2 or KCl powders.

The resonance of ^{125}Te nuclei was observed with Varian Unity 400 spectrometer with a 9.6 T super conducting magnet and Doty high temperature NMR probe, which utilizes a hot gas flow to heat up a specimen. The temperature was controlled by a digital temperature controller that could keep a temperature within $\pm 0.1°$ at a set point for a measurement. Since a thermocouple could not be placed in touch with a specimen, the actual temperature of a specimen was estimated by a set point which was converted to an specimen temperature by observing sudden increase in the resonance shift at the melting point of Te ($T_m = 724$ K) and the eutectic temperature of $Ge_{15}Te_{85}$, ($T_e = 648$ K). The accuracy of the temperature was estimated to be better than ± 5 K. The maximum temperature was limited at 833 K by the specification of the probe. In determining the ^{125}Te shift, the signal of ^{125}Te in a solution of TeO_2 in HCl was used as a standard. It was 123.3856 MHz. The spin-lattice relaxation time T_1 and spin–spin relaxation time T_2 were, respectively measured with the inversion-recovery ($\pi - \pi/2$) and the CPMG pulse sequences. The $\pi/2$ pulse was 5.3 μs and the number of transients was 5000–20 000 depending on a signal to noise ratio.

3. Experimental results

The resonance signals of ^{125}Te in liquid $Ge_{15}Te_{85}$ at three temperatures are shown in Fig. 1. It is clearly seen that the signal in liquid $Ge_{15}Te_{85}$ shifts to the lower frequencies with decreasing temperature. The dependences on temperature of the resonance shift, K^{125}, for both $Ge_{15}Te_{85}$ and pure Te are plotted in Fig. 2. The latter results are in reasonable agreement with those reported by Warren [7] in the overlapping temperature interval, where the isotropic chemical shift, $\sigma_{iso} = (6.2 \pm 0.5) \times 10^{-2}$%, was subtracted from his data for comparison. The rate of increase of K^{125} in liquid $Ge_{15}Te_{85}$ with increasing temperature becomes very large around T^*. At low temperatures, it approaches a constant value of about −0.07%. The temperature dependence of K^{125} in liquid Te appears much smaller than that in liquid $Ge_{15}Te_{85}$ although the deeply supercooled state below T^* could not be reached.

On molten $Ge_{15}Te_{85}$, we could measure T_1 and T_2 down to well below T^*, where molten $Ge_{15}Te_{85}$ is almost in a low temperature form. T_1 and T_2 are plotted in Fig. 3 as a function of temperature. In Te and $Ge_{15}Te_{85}$ at high temperatures both T_1 and T_2 almost coincide and our Te results agree with those of Warren [7] in the overlapping temperatures range. With decreasing temperature, T_1 and T_2 in liquid $Ge_{15}Te_{85}$ take a local maximum around T^*. At temperatures below T^*, T_1 passes through a local minimum and increases rapidly with decreasing temperature whereas T_2 decreases monotonously.

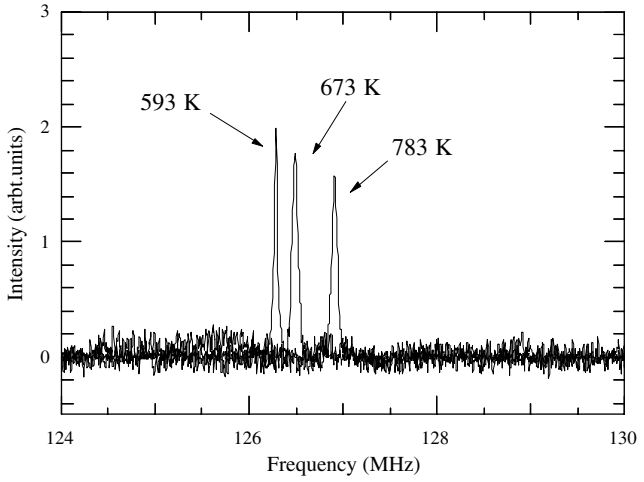

Fig. 1. Resonance signals of ^{125}Te nuclei in molten $Ge_{15}Te_{85}$ at three temperatures.