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Sub-millisecond ^{125}Te NMR spin-lattice relaxation times and large Knight shifts in complex tellurides: Validation of a quadratic relation across the spectrum

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ABSTRACT

^{125}Te NMR spectra and spin-lattice relaxation times, T_1, have been measured for several GeTe-based materials with Te excess. The spectra show inhomogeneous broadening by several thousand ppm and a systematic variation in T_1 relaxation time with resonance frequency. The quadratic dependence of the spin-lattice relaxation rate, $1/T_1$, on the Knight shift in the Korringa relation is found to be valid over a wide range of Knight shifts. This result confirms that T_1 relaxation in GeTe-based materials is mostly dominated by hyperfine interaction between nuclei and free charge carriers. In GeTe with 2.5% excess of Te, about 15% of the material exhibits a Knight shift of $\geq$4500 ppm and a T_1 of only 0.3 ms, indicating a high hole concentration that could correspond to close to 50% vacancies on the Ge sublattice in this component. Our findings provide a basis for determining the charge carrier concentration and its distribution in complex thermoelectric and phase-change tellurides, which should lead to a better understanding of electronic and thermal transport properties as well as chemical bonding in these materials.
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1. Introduction

Complex tellurides based on the GeTe narrow gap-band semiconductor exhibit interesting fundamental properties that enable their use as thermoelectric materials for conversion of heat to electricity [1–3] or phase-change materials for optical and electronic memory devices [4,5]. The free (mobile) charge carrier concentration is one of the most important parameters of these materials since it affects electronic and thermal properties of thermoelectric materials including tellurides [2]. It is well established that the high carrier concentration in GeTe is due to Ge vacancies with each vacancy generating two mobile holes in the valence band, i.e., GeTe is a self-doping semiconductor [6]. The Hall effect, typically used for determination of the carrier concentration, may not be sufficient in complex tellurides because they naturally are chemically and electronically inhomogeneous, as demonstrated by a scanning Seebeck microprobe [7] or by ^{125}Te nuclear magnetic resonance (NMR) [8–10]. ^{125}Te NMR has enabled us to study electronic inhomogeneity in various complex tellurides and to derive the carrier concentration via spin-lattice relaxation measurements [8,10].

The ^{125}Te resonance position $\delta_{total} = \delta_{chem} + K$ is determined by the chemical shift, δ_{chem}, reflecting the effect of the chemical environment, and the Knight shift, K, showing the influence of free charge carriers. The Knight shift and spin-lattice relaxation time T_1 are related via the Korringa relation [11,12]

$$K^2 T_1 T = \text{const} \quad (1)$$

where T is the absolute temperature. In addition, the spin-lattice relaxation time is related to the carrier concentration, p; experiment [10] and theory [12] show that at a given temperature, $T_1 \propto 1/p$. Combining these relations, one finds that the Knight shift and the charge carrier concentration at the same temperature are related through a quadratic relation

$$K^2/p = \text{const} \quad (2)$$

Hence, the ^{125}Te resonance position and the relations shown above can be used to estimate the carrier concentration and related electronic parameters of complex tellurides. The contributions from separate phases in GeTe-based materials with different carrier concentrations can significantly affect thermoelectric and

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other properties. If measurements of T_1 for all signals, including those with low intensity located far from the main peak, are possible, they may yield the distribution of local carrier concentration in multiphase materials and provide a basis for assessing the effect on electronic and thermal transport in tellurides. Here we report on ^{125}Te NMR data obtained for several GeTe-based materials. Inhomogeneous broadening by several thousand ppm due to different Knight shifts enables a test of the relation between K^2 and $1/T_1$ in a single sample. We show that such a relation holds over a wide range of ^{125}Te resonance frequencies and spin-lattice relaxation times.

2. Experimental

2.1. Samples synthesis and materials properties

Ingots (diameter 10 mm, length ~40 mm) of several alloys, stoichiometric GeTe and $Ag_{6.52}Sb_{6.52}Ge_{36.96}Te_{50}$ ("TAGS-85"), and $Ge_{48.8}Te_{51.2}$ ("GeTe+2.5% Te") and $Ag_{6.52}Sb_{6.52}Ge_{35.76}Te_{51.2}$ ("TAGS-85+2.5% Te") with Te excess (shown in at.%) were prepared by direct reaction of the constituent elements (Ge, Te, Ag, Sb) in fused quartz ampoules. The pressure in the ampoule was ~17 kPa; each ampoule with the constituent elements was heated up to 1325 K and periodically shaken to form a homogeneous melt. After ~4 h, the ampoule was cooled down with the furnace at a rate of 100 °C/h. The melt did not react with the walls of the silica ampoules and the ingots could be easily removed from the ampoule after cooling.

Each ingot was cut with a diamond saw and the resulting discs were used to prepare powder samples for crystal structure analysis by X-ray diffraction (XRD) and for ^{125}Te NMR measurements. For the nominally stoichiometric GeTe sample, the carrier (hole) concentration obtained from the Hall effect, $p = 8 \times 10^{20}$ cm^{-3}, the Seebeck coefficient, $S = +34\ \mu$VK^{-1}, and the electrical resistivity $\rho = 1.4\ \mu\Omega$ m at 300 K [10] were close to literature values [13,14]. For phase analysis, XRD patterns were obtained using a Scintag SDS diffractometer with Cu-K_α radiation. Densities were measured using the Archimedes method. The density of GeTe was 6.18 g cm^{-3} (literature value 6.14 g cm^{-3}) and 6.24 g cm^{-3} for neat Te. We obtained 6.22 g cm^{-3} for GeTe+2.5% Te and 6.46 g cm^{-3} for TAGS-85+2.5% Te (measured five times in two experiments, totally 10 times for each samples).

2.2. Nuclear magnetic resonance (NMR)

^{125}Te NMR experiments were performed at 126 MHz using a Bruker Biospin (Billerica, MA) DSX-400 spectrometer in a magnetic field of 9.39 T without sample spinning in 2.5-mm containers. The signal after a Hahn spin echo was measured with 2-μs excitation and 3-μs refocusing pulses. The latter was phase cycled, together with the receiver, according to the EXORCYCLE scheme [15], which provides the same refocusing as a π-pulse for any flip angle, at the expense of signal intensity (which is 50% for a π/2 refocusing pulse). ^{125}Te NMR chemical shifts were referenced to $Te(OH)_6$ in solution, and chemical shifts relative to $(CH_3)_2Te$ in benzene are larger by +712 ppm [9]. ^{125}Te NMR spin-lattice relaxation times were measured by saturation recovery; within the error margins, the relaxation at any analyzed specific point in the spectrum was exponential. In order to avoid distortion of the spectra by limited pulse and detection bandwidth, the excitation frequency was varied in 80-kHz steps across the spectrum; the envelope of the set of spectra is the minimally distorted line shape.

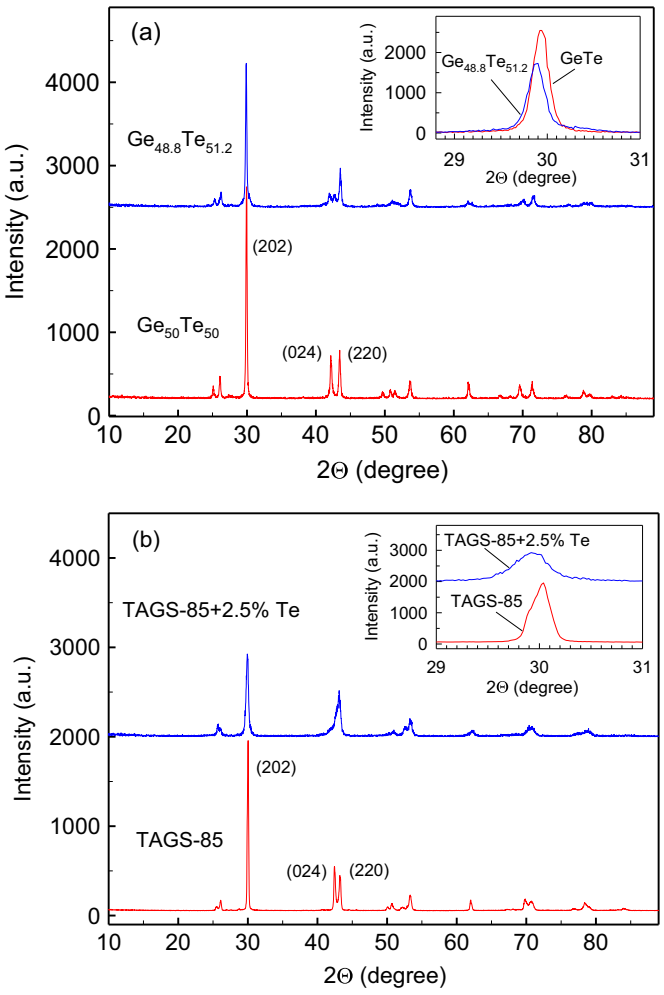

Fig. 1. XRD patterns of (a) GeTe and $Ge_{48.8}Te_{51.2}$ ("GeTe+2.5% Te"), and (b) $Ag_{6.52}Sb_{6.52}Ge_{36.96}Te_{50.0}$ ("TAGS-85") and $Ag_{6.52}Sb_{6.52}Ge_{35.76}Te_{51.2}$ ("TAGS-85+2.5% Te") at 300 K. The insets show an expanded view for the (202) main peak of all samples in the range of $29° \leq 2\Theta \leq 31°$.

3. Results and discussion

3.1. Crystal structure

XRD patterns of GeTe (Fig. 1(a)) and $Ag_{6.52}Sb_{6.52}Ge_{36.96}Te_{50}$ ("TAGS-85") (Fig. 1(b)), where Ge is partially replaced by [Ag+Sb] atoms [3,16], show that the alloys are single phase and have a similar crystal structure as reported earlier [9,16]. GeTe has a rhombohedral, i.e., slightly distorted cubic, crystal structure; lattice parameters obtained from neutron diffraction [17] and XRD [9] data are $a = b = c = 5.985$ Å and 5.980 Å, and rhombohedral angles are $\alpha = \beta = \gamma = 88.17°$ and 88.37°, respectively [9]. The main (202) peak is located at $2\Theta \approx 30°$ and the two-peak structure observed at $40° \leq 2\Theta \leq 45°$ is a signature of rhombohedral distortion [9,16,17]. The Te excess in $Ge_{48.8}Te_{51.2}$ ("GeTe+2.5% Te") slightly shifts the main peak [see inset on Fig. 1(a)] and results in the appearance of a third peak in the region of $40° \leq 2\Theta \leq 45°$.

XRD data for $Ag_{6.52}Sb_{6.52}Ge_{35.76}Te_{51.2}$ ("TAGS-85+2.5% Te") show that due to Te excess the (024) and (220) peaks move closer to each other, i.e., partially merge, and it is difficult to separate them (Fig. 1(b)). XRD data indicate that both GeTe+2.5% Te and TAGS-85+2.5% Te alloys have crystal structures similar to those of alloys without Te excess. The broad XRD patterns preclude a highly accurate determination of lattice parameters, but the increased width of the Bragg peaks is indicative of a distribution of lattice

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