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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Submitted to *Solid State Nuclear Magnetic Resonance*

Revised July 13, 2015

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 ≥ 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 provides 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.

Keywords: Complex tellurides; ^{125}Te NMR; Knight shift; spin-lattice relaxation; Korringa relation.

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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 $\delta_{\text{total}} = \delta_{\text{chem}} + K$ 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 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 their 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 $\text{Ag}_{6.52}\text{Sb}_{6.52}\text{Ge}_{36.96}\text{Te}_{50}$ (“TAGS-85”), and $\text{Ge}_{48.8}\text{Te}_{51.2}$ (“GeTe+2.5% Te”) and $\text{Ag}_{6.52}\text{Sb}_{6.52}\text{Ge}_{35.76}\text{Te}_{51.2}$ (“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 hours, the ampoule was cooled down with the furnace at a rate of 100 °C/hour. 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, $p = 8 \times 10^{20} \text{ cm}^{-3}$, the Seebeck coefficient, $S = +34 \text{ } \mu\text{VK}^{-1}$, and the electrical resistivity $\rho = 1.4 \text{ } \mu\Omega\text{m}$ at 300 K [9] 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 gcm^{-3} (literature value 6.14 gcm^{-3}) and 6.24 gcm^{-3} for neat Te. We obtained 6.22 gcm^{-3} for GeTe+2.5% Te and 6.46 gcm^{-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 $\pi/2$ refocusing pulse). ^{125}Te NMR chemical shifts were referenced to $\text{Te}(\text{OH})_6$ in solution, and chemical shifts relative to $(\text{CH}_3)_2\text{Te}$ 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.

3. Results and discussion

3.1. Crystal structure

XRD patterns of GeTe [Fig. 1(a)] and $\text{Ag}_{6.52}\text{Sb}_{6.52}\text{Ge}_{36.96}\text{Te}_{50}$ (“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 [9-8] data are $a = b = c = 5.985 \text{ \AA}$ and $5.980 \text{ \AA}$, and rhombohedral angles are $\alpha = \beta = \gamma = 88.17^\circ$ and 88.37° , respectively [9]. The main (202) peak is located at $2\Theta \approx 30^\circ$ and the two-peak structure observed at $40^\circ \leq 2\Theta \leq 45^\circ$ is a signature of rhombohedral distortion [9,16,17]. The Te excess in $\text{Ge}_{48.8}\text{Te}_{51.2}$ (“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 $40^\circ \leq 2\Theta \leq 45^\circ$.

XRD data for $\text{Ag}_{6.52}\text{Sb}_{6.52}\text{Ge}_{35.76}\text{Te}_{51.2}$ (“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 parameters, consistent with the structural inhomogeneity reflected in the broad NMR spectra (see below). Because Te excess in both GeTe and TAGS-85 affects the two-peak structure, we can suggest that it reduces the rhombohedral distortion, possibly due to an increase in the concentration of Ge vacancies. An insignificant amount of Te may form a

second phase as was reported for $\text{Ge}_x\text{Te}_{100-x}$ alloys [18]. A wide range of observed Knight shifts in a given sample allows us to use these materials for detection of ^{125}Te NMR signals and measure T_1 from Te in different chemical environments.

3.2. ^{125}Te NMR

The ^{125}Te NMR spectra of GeTe and GeTe+2.5% Te (Fig. 2), and TAGS-85 and TAGS-85 + 2.5% Te (Fig. 3) show quite different line shapes. GeTe shows one peak at +160 ppm [Fig. 2(a)] while the maximum of the TAGS-85 signal is at +150 ppm [Fig. 3(a)]. ^{125}Te NMR spectra of GeTe+2.5% Te and TAGS-85+2.5% Te show signal intensity over a wide frequency range, from about -500 to 4500 ppm.

^{125}Te NMR shows that in GeTe and TAGS-85, Te excess generally results in the appearance of asymmetric signals [Figs. 2(b) and 3(b)], i.e., some nuclei resonate at higher frequency (with positions to the left in the figure) compared to the major signal observed at about +150 ppm. Even a Te excess of only a few percent in GeTe may result in the appearance of a relatively high concentration of vacancies on the Ge sublattice and, therefore, free charge carriers (holes). Hence, the variations in K and T_1 connected via Eq. (1) can be achieved by additional Ge vacancies generated via added excess Te. The ^{125}Te NMR of GeTe + 2.5% Te shows large inhomogeneous broadening by thousands of ppm. This must be attributed to regions with different Knight shifts, which is confirmed by a gradual but pronounced decrease in T_1 with increasing resonance frequency (ppm value), from 5 ms at +160 ppm down to 0.3 ms at +4500 ppm (Fig. 2). The ^{125}Te NMR spectrum of TAGS-85 + 2.5% Te also shows a similar broadening, but over a slightly narrower range, and a decrease in T_1 from 3.2 ms at +160 ppm down to 0.4 ms at +3000 ppm (Fig. 3). Again this must be attributed to regions with different Knight shifts. As expected from Eq. (1),

a decrease in T_1 is accompanied by a paramagnetic (to larger positive values) Knight shift of the ^{125}Te resonance.

According to the $T_1 \propto 1/p$ relation [10,12], a reduction in spin-lattice relaxation time from 5.3 ms in GeTe to 0.3 ms in GeTe + 2.5% Te can be attributed to an increase in the carrier concentration, from $p = 8 \times 10^{20} \text{ cm}^{-3}$ to $p_{\text{max}} \sim 1.4 \times 10^{22} \text{ cm}^{-3}$. As mentioned above, the high charge carrier (hole) concentration in GeTe-based materials can be attributed to the high Ge vacancy concentration [6], not to doping with additional elements.

This situation is quite different from that observed for Si, where high electron or hole concentrations can be achieved via doping with B or P, respectively. However, the free carrier concentration in Si and tellurides can be estimated by ^{29}Si NMR [19,20] and by ^{125}Te NMR, respectively, via spin-lattice relaxation measurements [8,10,21]. Since each Ge vacancy in GeTe generates two holes [6], the hole concentration is twice the vacancy concentration. Based on $p_{\text{max}} \sim 1.4 \times 10^{22} \text{ cm}^{-3}$, the highest Ge vacancy concentration detected by ^{125}Te NMR in GeTe+2.5% Te can be estimated as $\sim 0.7 \times 10^{22} \text{ cm}^{-3}$, which corresponds to more than 50% of Ge vacancies on the Ge sublattice. Based on the hole concentration in our stoichiometric GeTe sample obtained from the Hall effect [9], the concentration of Ge vacancies in GeTe can be estimated as $4 \times 10^{20} \text{ cm}^{-3}$, which corresponds to about 4% Ge vacancies on the Ge sublattice. Our value is smaller than that reported for thin films, 10% for GeTe [22] and 8% for GeTe:Co [23]; these values indicate that the concentration of Ge vacancies in GeTe can be high.

Assuming that the same relation between hole and vacancy concentrations holds for the component in GeTe+2.5% Te with the highest hole concentration, $p_{\text{max}} \sim 1.4 \times 10^{22} \text{ cm}^{-3}$, detected by ^{125}Te NMR, the highest Ge vacancy concentration can be estimated as $\sim 0.7 \times 10^{22} \text{ cm}^{-3}$, which corresponds to about 50% of Ge vacancies on the Ge sublattice.

Note that this high value of Ge vacancies suggested by the very short T_1 value and large Knight shift involves only a small fraction, $\sim 15\%$, of the material. Therefore, the effect of the vacancy-rich component on chemical composition and lattice parameters of the entire sample will be moderate. It is difficult to directly test the presence of Ge vacancies using mass density measurements because the atomic mass of Ge is significantly smaller than that of Te. The mass density of GeTe is 6.14 gcm^{-3} , while that of Te is 6.24 gcm^{-3} , so a Te excess results in an increase of the mass density, which may cover the expected decrease due to Ge vacancies. Therefore, our density measurements by the Archimedes method remained inconclusive. However, support for the high carrier concentrations in GeTe+2.5% Te and TAGS-85+2.5% Te deduced by ^{125}Te NMR is provided by their smaller Seebeck coefficient compared to those in stoichiometric GeTe and TAGS-85: it is well known that a higher carrier concentration results in a smaller Seebeck coefficient [2].

In order to explain the high carrier concentration associated with short spin-lattice relaxation times of $1.1 \text{ ms} \geq T_1 \geq 0.3 \text{ ms}$ in both alloys with Te excess, we suggest that some Te atoms are surrounded by a combination of (i) 3 or 2 Ge atoms and 3 or 4 Ge vacancies, or (ii) 4 or 3 Ge atoms, 1 or 2 vacancies, and 1 Te atom. We propose that such fragments may exist in small volumes of the crystal lattice stabilized by surrounding regions with fewer Ge vacancies. Hence, ^{125}Te NMR data support the hypothesis that the change in the XRD two-peak structure near $2\Theta = 30^\circ$ resulting from Te excess in both GeTe and TAGS-85 can be attributed to an increase in vacancies on the Ge sublattice. Since both the NMR spectrum and the change in spin-lattice relaxation time reflect the distribution of charge carrier concentration, NMR can detect the presence of high-vacancy regions even when they are not the dominant component. Nevertheless, the surprising conclusion about a high Ge vacancy concentration in some regions in GeTe+2.5%

Te and TAGS-85+2.5% Te alloys forced upon us by the ^{125}Te NMR T_1 and Knight shift data is a hypothesis that needs to be confirmed by other methods.

Note that no signal in the ^{125}Te NMR spectra indicates the presence of bulk Te, which is expected to have a low carrier concentration and a spin-lattice relaxation time on the order of tens of milliseconds [12]. This indicates that the amount of tellurium in GeTe+2.5% Te and TAGS-85+2.5% Te alloys forming a nearly neat second phase is insignificant.

The dependence of spin-lattice relaxation rate, $1/T_1$, (Fig. 4) on the resonance frequency is plotted for two samples, GeTe+2.5% Te and TAGS-85+2.5% Te; points for GeTe ($T_1 = 5.3$ ms and resonance position of +160 ppm [9,10]), TAGS-85 ($T_1 = 3.1$ ms and +150 ppm [16]), as well as $\text{Ge}_{46}\text{Bi}_4\text{Te}_{50}$ ($T_1 = 10$ ms and -240 ppm [10]) are also included. Replacement by Ge in GeTe by Bi increases T_1 , i.e., it reduces the carrier concentration.

3.3. Validation of the quadratic relation between K and $1/T_1$

The ^{125}Te NMR data can be fit by the quadratic relation (Eq. 1) generalized at a given temperature in the form $1/T_1 = cK^2 = c(\delta_{\text{total}} - \delta_{\text{chem}})^2$ with average chemical shifts of $\delta_{\text{chem}} = -1030$ and -1236 ppm and coefficients $c_{\text{GeTe}} = (1.25 \pm 0.1) \times 10^{-7} \text{ ms}^{-1} \text{ ppm}^{-2}$ and $c_{\text{TAGS-85}} = (1.43 \pm 0.1) \times 10^{-7} \text{ ms}^{-1} \text{ ppm}^{-2}$ for GeTe- and TAGS-85-based alloys, respectively (see Fig. 4). The difference in the coefficients as well as in the average chemical shifts of GeTe and TAGS-85 can be attributed to the effect of [Ag+Sb] atoms replacing Ge in GeTe. The relation between K^2 and $1/T_1$ proves that the hyperfine coupling between the charge carriers and nuclei is the dominant relaxation mechanism in GeTe-based materials, including the well-known high efficiency Ag-Sb-Ge-Te (TAGS) thermoelectric materials, and confirms that T_1 can be used to determine the carrier concentration using the relation $p = 4.24 \times 10^{21} \text{ cm}^{-3} \text{ ms}/T_1$ [10]. The GeTe chemical shift of -1030

ppm (± 100 ppm) obtained from this analysis agrees within the error margins with our previous estimate of -890 ppm (± 150 ppm) [24].

Hence, our ^{125}Te NMR data confirm that the major ^{125}Te T_1 relaxation mechanism in these complex tellurides independently of local composition is determined by hyperfine interaction between nuclei and free charge carriers. Eq. (2) connecting the Knight shift and carrier concentration in complex tellurides is, generally, valid over wide ranges of both values. By measurements of resonance frequency and spin-lattice relaxation it is possible to derive the local carrier concentration, calculate the Knight shift, and estimate the chemical shift. This provides unique opportunities to better understand electronic and thermal transport properties as well as chemical bonding in complex thermoelectric and phase-change tellurides.

ACKNOWLEDGMENTS

The authors wish to thank L.L. Jones and H. Sailsbury (Materials Preparation Center at Ames Laboratory U.S. Department of Energy) for materials synthesis. This work was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering and performed at the Ames Laboratory, which is operated for the U.S. Department of Energy by Iowa State University under Contract No DE-AC02-07CH11358.

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FIG. 1. XRD patterns of (a) GeTe and $\text{Ge}_{48.8}\text{Te}_{51.2}$ (“ $\text{GeTe} + 2.5\% \text{ Te}$ ”), and (b) $\text{Ag}_{6.52}\text{Sb}_{6.52}\text{Ge}_{35.76}\text{Te}_{51.2}$ (“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 $29^\circ \leq 2\Theta \leq 31^\circ$.

FIG. 2. ^{125}Te NMR spectra of (a) GeTe and (b) $\text{Ge}_{48.8}\text{Te}_{51.2}$ ("GeTe + 2.5% Te"). The thin lines show a series of spectra measured with different carrier frequencies, systematically incremented in 80-kHz steps. The thick line is the envelope of the spectra, which approximates the true, undistorted spectrum. Spin-lattice relaxation times are given in (b) for several frequency positions.

FIG. 3. ^{125}Te NMR spectra of (a) of $\text{Ag}_{6.52}\text{Sb}_{6.52}\text{Ge}_{36.96}\text{Te}_{50.0}$ (“TAGS-85”) and (b) $\text{Ag}_{6.52}\text{Sb}_{6.52}\text{Ge}_{35.76}\text{Te}_{51.2}$ (“TAGS-85 + 2.5% Te”). Thin lines: spectra measured with different carrier frequencies. Thick line: envelope of the spectra, approximating the true, undistorted spectrum. Spin-lattice relaxation times are given in (b) for several different frequency positions.

FIG. 4. Dependence of the spin-lattice relaxation rate, $1/T_1$, on the ^{125}Te resonance position in the spectra of GeTe- and TAGS-85-based alloys with Te excess in Fig. 2(b) and Fig. 3(b); points for stoichiometric GeTe and TAGS-85 as well as $\text{Ge}_{46}\text{Bi}_4\text{Te}_{50}$ [10] are also included (near 0 ppm). The fit curves are based on the generalized Korringa relation with fitting coefficients (see text) of $c_{\text{GeTe}} = (1.25 \pm 0.1) \times 10^{-7} \text{ ms}^{-1}\text{K}^{-2}$ (red curve) and $c_{\text{TAGS-85}} = (1.43 \pm 0.1) \times 10^{-7} \text{ ms}^{-1}\text{K}^{-2}$ (black curve).

Graphical Abstract

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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