Electronic properties of GeTe and Ag- or Sb-substituted GeTe studied by low temperature $^{125}$Te NMR

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We have carried out $^{125}$Te nuclear magnetic resonance (NMR) in a wide temperature range of 1.5 – 300 K to investigate electronic properties of Ge$_{50}$Te$_{50}$, Ag$_2$Ge$_{48}$Te$_{50}$ and Sb$_2$Ge$_{48}$Te$_{50}$ from a microscopic point of view. From the temperature dependence of NMR shift ($K$) and nuclear spin lattice relaxation rate ($1/T_1$), we found that two bands contribute to the physical properties of the materials. One band overlaps the Fermi level providing the metallic state where no strong electron correlations are revealed by Korringa analysis. The other band is separated from the Fermi level by an energy gap of $E_g/k_B \sim 67$ K, which gives rise to the semiconductor-like properties. First-principle calculation reveals that the metallic band originates from the Ge vacancy while the semiconductor-like band is related to the fine structure of the density of states near the Fermi level. Low-temperature $^{125}$Te NMR data for the materials studied here clearly show that the Ag substitution increases hole concentration while Sb substitution decreases it.

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I. INTRODUCTION

Complex tellurides have been studied extensively due to their intriguing fundamental properties and their application as thermoelectric materials,1–6 which directly convert heat into electricity. The efficiency is characterized by the dimensionless figure of merit $zT = S^2\sigma T/\kappa$ (S the Seebeck coefficient, $\sigma$ the electrical conductivity, $T$ the absolute temperature, and $\kappa$ the thermal conductivity). The well-known group of thermoelectric materials, the complex tellurides based on GeTe,7–9 TAGS-m materials (GeTe)$_m$(AgSbTe$_2$)$_{100-m}$, have a thermoelectric figure of merit $zT$ above 1.6,10–12. According to band calculations, GeTe is a narrow-band-gap semiconductor whose band gap is calculated to be 0.3 – 0.5 eV.13–16 On the other hand, electrical resistivity measurements show metallic behavior,7,17–20 although a small gap also has been observed by optical measurements.21 This is believed to be due to high hole concentrations generated by Ge vacancies, forming a self-dopant system with $p$-type conductivity.7,17,22 Therefore, depending on the samples’ composition, they may have different concentrations of Ge vacancies resulting in different physical properties. This makes it very difficult to understand physical properties of GeTe-based materials. In fact, there is a significant discrepancy between the electronic and thermal transport data for GeTe-based materials reported in the literature.5,23–25

To avoid such confusion, one needs to study the physical properties using well characterized samples. We have conducted systematic characterization of GeTe by using x ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), Seebeck coefficient, electrical resistivity, Hall effect, thermal conductivity, and $^{125}$Te nuclear magnetic resonance (NMR) measurements.7 Hereafter, we will use notation Ge$_{50}$Te$_{50}$ for GeTe with the coefficients shown in atomic percent.

In our previous paper,7 we concluded that the discrepancy in the data for Ge$_{50}$Te$_{50}$ reported in literature can be attributed to the variation in the Ge/Te ratio of solidified samples as well as to different conditions of measurements. It is well established that NMR is a powerful tool to investigate carrier concentrations in semiconductors from a microscopic point of view. The Hall and Seebeck effects show only bulk properties, which can be affected by small amounts of a second phase.26,27 Nuclear spin lattice relaxation rates ($1/T_1$) have been measured at room temperature, and were found to increase linearly with carrier concentrations.28 However, to our knowledge, no systematic NMR investigation of Ge$_{50}$Te$_{50}$ has been carried out over a wide temperature range.

In this paper, we report the first $^{125}$Te NMR measurements of Ge$_{50}$Te$_{50}$ over a wide temperature range of $T = 1.5 - 300$ K. We found that the NMR shift $K$ and $1/T_1$ data are nearly temperature-independent at temperatures below $\sim 50$ K and both increase slightly with increasing temperature at high temperatures. These behaviors can be explained well by a two-band model where one band overlaps the Fermi level and the other band is separated from the Fermi level by an energy gap of $E_g/k_B \sim 67$ K. First-principle calculations indicate that the first band originates from the Ge vacancy while the second band is related to the fine structure of the density of states near the Fermi level. We also carried out $^{125}$Te NMR measurements of M$_2$Ge$_{48}$Te$_{50}$ (M = Ag, Sb) to study carrier doping effects on electronic properties. Clear changes in carrier concentration upon Ag or Sb substitutions were observed: the Ag substitution increases the hole concentration whereas Sb substitution decreases the concentration, which is consistent with our previous report.29
can be observed below in independent of temperature although a slight increase measured at 4.3 K for Ge

The inset shows the temperature dependence of FWHM for the samples.

II. EXPERIMENTAL

Polycrystalline samples of Ge<sub>50</sub>Te<sub>50</sub>, Ag<sub>2</sub>Ge<sub>48</sub>Te<sub>50</sub> and Sb<sub>2</sub>Ge<sub>48</sub>Te<sub>50</sub> were prepared by direct reaction of the constituent elements of Ge, Te, Ag or Sb in fused silica ampoules, as described in Ref. 7 and Ref. 29. The samples were well characterized by XRD, Seebeck coefficient, electrical resistivity, Hall effects, and room temperature <sup>125</sup>Te NMR measurements. The coarsely powdered samples were loosely packed into 6-mm quartz tubes for NMR measurements. NMR measurements of <sup>125</sup>Te (I = 1<sup>⁄</sup>2; 2<sub>γ</sub><sup>T</sup> = 13.464 MHz/T) were conducted using a homemade phase-coherent spin-echo pulse spectrometer. <sup>125</sup>Te NMR spectra were obtained either by Fourier transform of the NMR echo signal at a constant magnetic field of 7.4089 T or by sweeping the magnetic field at a frequency of 99.6 MHz in the temperature range of T = 1.5 - 300 K. The NMR echo signal was obtained by means of a Hahn echo sequence with a typical π/2 radiofrequency (rf) pulse length of 7.5 μs which produces an oscillation field (so-called H<sub>1</sub>) of ~ 25 Oe.

III. RESULTS AND DISCUSSION

Figure 1 shows field-swept <sup>125</sup>Te NMR spectra measured at 4.3 K for Ge<sub>50</sub>Te<sub>50</sub>, Ag<sub>2</sub>Ge<sub>48</sub>Te<sub>50</sub> and Sb<sub>2</sub>Ge<sub>48</sub>Te<sub>50</sub>. The full width at half maximum (FWHM) for Ge<sub>50</sub>Te<sub>50</sub> is 40.0(5) Oe at T = 4.3 K which is almost independent of temperature although a slight increase can be observed below ~ 25 K as shown in the inset of Fig. 1. This FWHM is slightly smaller than 43 Oe at room temperature reported previously. While the peak position slightly shifts to higher magnetic field, the peak position slightly shifts to higher magnetic field with Sb substitution. The FWHM shows a slight increase to 56.0(5) Oe and 54.0(5) Oe at T = 4.3 K for Ag- or Sb-substituted samples, respectively. The FWHM is also found to increase slightly with decreasing temperature for Ag- or Sb-substituted samples. These observed values are also close to the values (~ 50 Oe) at room temperature reported previously.

The temperature dependence of K is shown in Fig. 2 where K is determined by the peak position of the spectrum. Although the absolute values of K depend on the sample composition, their temperature dependencies exhibit qualitatively the same behavior: K slightly decreases with decreasing temperature, then levels off at low temperatures. The temperature dependence of K can be analyzed by a two-band model where the first band overlaps the Fermi level and the second band is separated from the Fermi level by an energy gap (E<sub>g</sub>). The nearly temperature-independent behavior observed at low temperatures is a typical characteristic of metals (due to Pauli paramagnetic susceptibility) originated from the first band. The increase of K at high temperatures originates from the second band, similar to the case of semiconductors. Thus, the total NMR shift is given by

\[ K = K_{\text{Pauli}} + K_{\text{semi}} + K_{\text{orb}} \]  

where K<sub>Pauli</sub> is the temperature-independent NMR shift related to the the Pauli paramagnetic susceptibility due to self-doping/substitution effects and K<sub>semi</sub> originates from the semiconducting-like nature giving rise to the temperature-dependent contribution because of thermal excitations across an energy gap E<sub>g</sub>. The temperature-independent K<sub>orb</sub> includes chemical shift, orbital and Landau diamagnetic contributions. As is shown below, K<sub>orb</sub> is estimated to be ~0.142(10)%.

![FIG. 1: (Color online) Field-swept <sup>125</sup>Te-NMR spectra for Ge<sub>50</sub>Te<sub>50</sub>, Ag<sub>2</sub>Ge<sub>48</sub>Te<sub>50</sub> and Sb<sub>2</sub>Ge<sub>48</sub>Te<sub>50</sub> at \( f = 99.6 \text{ MHz} \) and \( T = 4.3 \text{ K} \). The dotted vertical line is a guide for eyes. The inset shows the temperature dependence of FWHM for the samples.](image)

![FIG. 2: (Color online) Temperature dependence of NMR shift K for for Ge<sub>50</sub>Te<sub>50</sub> (red circles), Ag<sub>2</sub>Ge<sub>48</sub>Te<sub>50</sub> (green squares) and Sb<sub>2</sub>Ge<sub>48</sub>Te<sub>50</sub> (blue triangles). The solid lines are best fits using Eq. 2.](image)
the temperature-dependent constant value originates from the conduction carriers and the second term is due to thermal excitation effects from the second band.\textsuperscript{31,32} Here we assumed in the simple model (Eq. 3) that a cross-relaxation effect originated from mixing of the two bands is negligible for simplicity. A similar analysis of the temperature dependence of $1/T_1 T$ without the cross-relaxation process has been reported in the semimetal CaAl$_2$-$x$Si$_{2+x}$ (Ref. 33) and in the Heusler-type compound Fe$_2$Co$_{1-x}$V$_{1-x}$Al (Ref. 34). Using Eq. 3, the magnitude of $E_g$ is estimated to be 67(4) K for Ge$_{50}$Te$_{50}$ and Ag$_{2}$Ge$_{48}$Te$_{50}$, although the experimental data are somewhat scattered, as shown in Fig. 3(c) where $[(1/T_1 T) - (1/T_1 T)_{\text{const}}]/T$ is plotted against to $1/T$ on a semi-log scale. It is difficult to estimate $E_g$ for Sb$_2$Ge$_{48}$Te$_{50}$ due to a large scattering of the data. The black solid line in the figure is the best fit with a assumption of $E_g/k_B = 67$ K, which seems to reproduce the data reasonably although we cannot determine $E_g$.

It is noted that 67 K is too small to attribute to the semiconducting gap energy of 0.3 – 0.5 eV reported from optical measurements for GeTe.\textsuperscript{21}

The solid lines in Fig. 3(a) are best fits to Eq. 3, using $E_g/k_B = 67$ K, with $(1/T_1 T)_{\text{const}} = 0.37$ (sK)$^{-1}$, $A = 0.0013$ (sK$^2$)$^{-1}$ for Ge$_{50}$Te$_{50}$, $(1/T_1 T)_{\text{const}} = 0.90$ (sK$^2$)$^{-1}$ for Ge$_{50}$Te$_{50}$, $(1/T_1 T)_{\text{const}} = 0.33$ (sK$^2$)$^{-1}$, $A = 0.00068$ (sK$^2$)$^{-1}$ for Sb$_2$Ge$_{48}$Te$_{50}$, respectively. Within a Fermi liquid picture, $(1/T_1 T)_{\text{const}}$ is proportional to the square of the density of states at the Fermi level $N(E_F)$ and $K_{\text{Pauli}}$ is proportional to $N(E_F)$. Therefore, as $K_{\text{Pauli}}$ is expected to be proportional to $(1/T_1 T)_{\text{const}}$, one can estimate the temperature-independent $K_{\text{orb}}$ by plotting $(1/T_1 T)_{\text{const}}$ as a function of the temperature-independent $K = K_{\text{Pauli}} + K_{\text{orb}}$ at low temperatures for different samples. As shown in Fig. 4, we actually found a linear relation between $(1/T_1 T)_{\text{const}}$ and $K$ in the plot of $(1/T_1 T)_{\text{const}}$ vs. the temperature-independent $K$, from which $K_{\text{orb}}$ is estimated to be $-0.142(10)$%.

Using the NMR data, we can discuss electron correlations through the Korringa ratio analysis. As described, both $(1/T_1 T)_{\text{const}}$ and $K_{\text{Pauli}}$ are determined primarily by $N(E_F)$. This leads to the general Korringa relation

$$T_1 T K_{\text{spin}}^2 = \frac{\hbar}{4\pi^2 k_B} \left( \frac{c}{\gamma N} \right)^2 = \frac{R}{\gamma N}$$

where $K_{\text{spin}}$ denotes the spin part of the NMR shift. For the $^{125}$Te nucleus, $R = 2.637 \times 10^{-6}$ Ks. Deviations from $R$ can reveal information about electron correlations in materials, which are conveniently expressed via the Kor-
ringa ratio \( \alpha \equiv R/(T_1 T K_{\text{spin}}^2) \). For uncorrelated metals, one has \( \alpha \sim 1 \). For antiferromagnetic spin correlation, \( \alpha >> 1 \); in contrast, \( \alpha << 1 \) for ferromagnetic spin correlations. The Korringa ratio \( \alpha \), then, reveals how electrons correlate in materials. Figure 5 shows the temperature dependence of \( \alpha \) for the three samples. We found the values of \( \alpha \) for all samples are similar, \( \alpha \sim 1.25 \) at low temperatures, where the temperature-independent \((1/T_1 T)_{\text{const}}\) and \( K_{\text{Pauli}} \) dominate, indicative of no strong correlations for conduction carriers originated from self-doping/substitution effects in the samples. With increasing temperature, \( \alpha \) slightly increases above \( \sim 50 \) K. If we assume that the Korringa relation holds at high temperatures, the increase suggests a tiny enhancement of antiferromagnetic spin correlations for carriers. Since the temperature dependence of \( \alpha \) originates from the second band having semiconducting nature, these results may suggest that thermally excited carriers play an important role in electron correlation effects in the system. As electron correlations have been pointed out to be significant for a figure of merit (\( zT \) values), it is interesting if the increase of \( zT \) in Ge\(_{50}\)Te\(_{50}\) at high temperatures above 300 K\(^2\) is related to the electron correlations. Further NMR studies at high temperatures above 300 K are required in shedding light on the relationship between electron correlations and \( zT \), which is currently in progress.

We now discuss how the carrier concentration changes by Ag or Sb substitution based on \( N(E_F) \) obtained from NMR data. In a parabolic band for noninteracting carriers, \( N(E_F) \) is given by \( N(E_F) = \frac{4\pi}{\hbar^2} (2m^*)^{3/2} E_F^{1/2} \) where \( E_F = \frac{h^2}{2m^*} (3\pi^2 n)^{2/3} \). Here \( n \) is the carrier concentration and \( m^* \) the renormalized effective carrier mass. Therefore, one can get a simple relation of \( N(E_F) \propto (m^* n)^{1/3} \). From the values of \((1/T_1 T)_{\text{const}}\) and/or \( K_{\text{Pauli}} \), the effect from \( m^* \) can be negligible, the carrier concentration in Ag\(_{2}\)Ge\(_{48}\)Te\(_{50}\) is found to increase about 380\% from that of Ge\(_{50}\)Te\(_{50}\) while the carrier concentration in Sb\(_{2}\)Ge\(_{48}\)Te\(_{50}\) is reduced only by \( \sim 16\% \). Since there are 1.85\( \times 10^{22} \) cm\(^{-3} \) Ge atoms in Ge\(_{50}\)Te\(_{50}\), the replacement of two Ag atoms for two Ge atoms out of 50 provides additional 7.4\( \times 10^{20} \) cm\(^{-3} \) holes into the system. On the other hand, the substitution of two Sb atoms should reduce the same amount of carrier concentration (7.4\( \times 10^{20} \) cm\(^{-3} \)). Therefore, the large increase of the carrier concentration by Ag substitution and the slight decrease of that by Sb substitution cannot be explained by the simple substitution effect. These results strongly indicate that the number of Ge vacancies must be different for Ag or Sb substitutions. A similar conclusion has been pointed out in our previous paper.

To obtain insight into the origin of the metallic conductivity in Ge\(_{50}\)Te\(_{50}\), particularly the vacancies effects on electronic structure of Ge\(_{50}\)Te\(_{50}\), we performed first-principles calculations where we employed a full-potential linear augmented plane wave method (FP-LAPW)\(^{38}\) with a generalized gradient approximation (GGA) functional.\(^{39}\) We constructed supercells which are composed of 27 Ge atoms and 27 Te atoms and randomly chose sites for vacancies or for Ag substituted site. For obtaining self-consistent charge density, we employed \( R_{\text{MT}} k_{\text{max}} = 7.0 \) and \( R_{\text{MT}} = 2.3 \) and 2.8 a.u. for Ge and Te atoms respectively. We selected 828 k-points in irreducible brillouin zone for obtaining self-consistent charge and density of states (DOS). As convergence criteria, we used energy difference 0.0001 Ry/cell, charge difference 0.0001 e, and force difference 1.0 mRy/a.u. between self-consistent steps. To get an optimized structure, we relaxed atoms around the vacancy or the substituted atom so that forces on each atom are less than 2.0 mRy/a.u.

Figure 6(a) shows the calculated DOS for a perfect Ge\(_{27}\)Te\(_{27}\) without any defect, with a band gap of \( \sim 0.5 \)
FIG. 6: (Color online) Density of states (DOS) near the Fermi level ($E_F$). Black line is the total DOS. In some figures, atomic decomposed DOS is shown where the blue and red dotted lines show DOS from Te $5p$ and Ge $4p$ electrons, respectively: (a) Ge$_{27}$Te$_{27}$, (b) Ge$_{26}$Te$_{27}$, (c) Ge$_{27}$Te$_{26}$, (d) (Ge$_{26}$Ag)Te$_{27}$, (e) Ge$_{27}$ (Te$_{26}$Ag), and (f) (Ge$_{26}$Ag)Te$_{26}$.

eV (semiconductor nature). This agrees well with previous reports $^{15,16,20}$ Here we show atomic decomposed DOS of the perfect Ge$_{27}$Te$_{27}$, where the black line shows the total DOS. The red and blue dotted lines show DOS from Te $5p$ and Ge $4p$ electrons, respectively. Figures 6(b) and 6(c) show the vacancy effect on DOS. In the case of a vacancy at the Ge site (Ge$_{26}$Te$_{27}$), the Fermi level $E_F$ moves to lower energy while keeping a similar gap structure to the case of Ge$_{27}$Te$_{27}$. This produces a finite DOS at $E_F$, giving rise to metallic character. The most part of DOS at $E_F$ originates from Te $5p$ and Ge $4p$ electrons. On the other hand, a vacancy at the Te site (Ge$_{27}$Te$_{26}$) keeps semiconducting states although some isolated states are developed in the gap. We conclude that a vacancy at the Ge site gives rise to $p$-type metallic conductivity in Ge$_{50}$Te$_{50}$ as has been observed in experiments. A similar conclusion based on electronic structure calculations has been reported by Edwards et al. $^{20}$ We further investigate the Ag substitution effect on electronic states. Figures 6(d) and 6(e) show a Ag atom substitution effect on DOS. While replacing a Ge atom by a Ag atom lowers the Fermi level and gives metallic character as in the case of a Ge vacancy, replacing a Te atom develops some isolated states in the gap and places $E_F$ on the isolated states. Finally, Fig. 6(f) shows DOS for a case that a Ag atom replaces a Ge atom and a vacancy on a the Te atom site. In this case the impurity states are sharper than other cases and $E_F$ is located at the center of isolated states. As we discussed, our NMR data were well explained by the two-band model where one band overlaps the Fermi level giving metallic nature and the other band is separated from the Fermi level by an energy gap of $E_g/k_B = 67(4)$ K. It is clear that the metallic band can be attributed to the Ge vacancy effect, while the second band cannot be explained by the effect. We found that a vacancy at the Te sites produces an isolated state in the gap, and one may think that it could be the origin of the second band. However, our observation of a gap magnitude of 67(4) K $^{[5.8(3) \, \text{meV]}}$ is much smaller than the gap energy of order (0.1 eV) even if we take the isolated states created by the Te defects into consideration. Therefore, we consider that the observed semiconducting nature cannot be attributed to the Te-defect effects but probably fine structures of DOS near the Fermi level.

Finally it is interesting to point out the inhomogeneity of the electronic states in the samples. According to Levin et al., $^{28}$ electronic inhomogeneity has been observed in some semiconductors such as PbTe from $1/T_1$ measurements. We investigate homogeneity of electronic states in the samples by measuring $1/T_1$ at $T = 4.3$ K and different positions in the spectra for the three samples. As shown in Figs. 7 (a)-(c), $1/T_1$ seems to depend on the position in the spectrum, where we plotted $1/T_1$ together with the corresponding spectrum. Here, it is noted that, since our $H_1$ for $T_1$ measurements is $\sim 25$ Oe which is much smaller than the line width of the observed spectrum, we cannot saturate the whole spectrum with the single $rf$ pulse. What we have measured is an average value of $T_1$ for a part of the line saturated by the $rf$ pulse. For each position, we observed a nearly single exponential behavior in nuclear recovery. This is probably due to a small distribution of $T_1$ in the saturated part of the line, although $T_1$ depends on position in the spectrum.
carrier concentrations in Ge. Inhomogeneous distribution of defects creating areas with differing carrier concentrations can be estimated from the distribution of NMR shift, \( \Delta K / K_{\text{spin}} \), where \( \Delta K \) was estimated from the FWHM of the NMR spectrum at \( T = 4.3 \) K. From the relation of \( \Delta n / n = (\Delta K / K_{\text{spin}})^3 \), \( \Delta n / n \) are estimated to be 0.25, 0.17, and 0.67, for Ge\(_{50}\)Te\(_{50}\), Ag\(_{2}\)Ge\(_{48}\)Te\(_{50}\), and Sb\(_{2}\)Ge\(_{48}\)Te\(_{50}\), respectively. Using the average local carrier concentration \( n = 8.0 \times 10^{20} \) cm\(^{-3}\) (Ge\(_{50}\)Te\(_{50}\)), 1.7 \times 10^{20} \) cm\(^{-3}\) (Ag\(_{2}\)Ge\(_{48}\)Te\(_{50}\)) and 4.0 \times 10^{20} \) cm\(^{-3}\) (Sb\(_{2}\)Ge\(_{48}\)Te\(_{50}\)) obtained from the Hall coefficient measurement, \( 3 \Delta n \) are estimated to be 2.0 \times 10^{20} \) cm\(^{-3}\), 2.9 \times 10^{20} \) cm\(^{-3}\), and 2.7 \times 10^{20} \) cm\(^{-3}\), respectively.

IV. CONCLUSION

We have carried out \(^{125}\)Te NMR measurements to microscopically investigate the electronic properties of Ge\(_{50}\)Te\(_{50}\), Ag\(_{2}\)Ge\(_{48}\)Te\(_{50}\) and Sb\(_{2}\)Ge\(_{48}\)Te\(_{50}\). For Ge\(_{50}\)Te\(_{50}\), the NMR shift \( K \) and \( 1/T_1 T \) data are nearly temperature independent at low temperatures below \( \sim 50 \) K and both increase slightly with increasing temperature at high temperatures. These behaviors are well explained by a two-band model where one band overlaps the Fermi level and the other band is separated from the Fermi level by an energy gap of \( E_g / k_B = 67(4) \) K. Korringa analysis indicates that the conduction carriers can be considered as free carriers with no significant electron correlations at low temperatures. On the other hand, Korringa ratio increases slightly at high temperature, suggesting the slight enhancement of the electron correlation. A first-principle calculation revealed that the metallic band originates from the Ge vacancy while the semiconductor-like band may be related to the fine structure of the density of states near the Fermi level. Low-temperature \(^{125}\)Te NMR data for Ag\(_{2}\)Ge\(_{48}\)Te\(_{50}\) and Sb\(_{2}\)Ge\(_{48}\)Te\(_{50}\) clearly demonstrate that the carrier concentration changes by Ag or Sb substitutions where the Ag substitution increases hole concentration while Sb substitution decreases the concentration.

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