

Probing mixed valence states by nuclear spin-spin relaxation time measurements

Y. Ihara^{1,*}, M. Shimohashi,¹ and M. Kriener^{2,†}¹*Department of Physics, Faculty of Science, Hokkaido University, Sapporo 060-0810, Japan*²*RIKEN Center for Emergent Matter Science (CEMS), Wako 351-0198, Japan*

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Several elements in the periodic table exhibit an interesting and often overlooked feature: They skip certain valence states, which is discussed in the field of superconductivity to be in favor of fostering higher transition temperatures T_c . However, from the experimental point of view, it is often deemed difficult to probe changes in the valence state. Here we demonstrate that the latter are accessible by the spin-spin relaxation rate $1/T_2$ in nuclear magnetic resonance. As target material, we chose the solid solution $\text{Ge}_{1-x}\text{In}_x\text{Te}$, where valence-skipping In induces superconductivity and changes its valence state as a function of x . We observe a strong enhancement in $1/T_2(x)$ and, most importantly, find that $1/T_2$ and T_c exhibit a strikingly similar x dependence. These results underline the importance of valence physics for the evolution of superconductivity in $\text{Ge}_{1-x}\text{In}_x\text{Te}$. A model based on a Ruderman-Kittel-Kasuya-Yosida type of interaction among the In nuclei is proposed which fully accounts for the experimental results.

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The valence-skipping degree of freedom is observed in several elements, such as Bi, Sn, In, Tl among others. As an example, in prototypical BaBiO_3 a Bi ion should take its $4+$ state which means that a single electron occupies the $6s$ shell. This situation is known to be energetically unfavorable. Therefore Bi is considered to appear as a mixture of Bi^{3+} and Bi^{5+} in BaBiO_3 and, hence, Bi^{4+} is the *skipped* valence state. It was Varma [1] who first pointed out that this feature may be responsible for the high-temperature superconductivity (transition temperature $T_c \sim 30$ K) observed in K-doped BaBiO_3 [2]. However, to date there is no unambiguously clear experimental evidence that valence skipping indeed supports superconductivity although quite some experimental and theoretical work on various materials has been done over the years [3–19]. Apparently, one obstacle is the difficulty to capture the changes in the valence state as a function of an external parameter such as doping. Among the methods employed are photoemission spectroscopy (PES), x-ray emission spectroscopy, Mössbauer spectroscopy, or the spin-lattice relaxation rate $1/T_1$ in nuclear magnetic resonance (NMR) [4,7,18,20–23]. Since the energies of the different involved valence states are usually close to each other, the measured spectra are often broad and difficult to split quantitatively, complicating their interpretation. Against this background, we propose to measure the NMR spin-spin relaxation rate $1/T_2$ rather than $1/T_1$ to study valence-state physics in solid

solutions, which is rather sensitive to the valence-mixing induced disorder, i.e., the degree of mixture of the different valence states. To demonstrate the strength of this technique, we chose chemically simple $\text{Ge}_{1-x}\text{In}_x\text{Te}$ as target material which has been reported to superconduct and where In is the valence-skipping element [21,24]: When introduced into GeTe with the formal valence state Ge^{2+} (cf. Refs. [16,25] for this nomenclature), In replaces Ge^{2+} and, hence, should also appear in the same valence state. However, In^{2+} is energetically unstable which creates the anticipated competition of its monovalent and trivalent states.

In Ref. [21], it is argued that initially trivalent In enters GeTe. In starts to appear also in its monovalent state when traversing $x \sim 0.12$, and the majority of the dopants become monovalent at intermediate $x \sim 0.4$. The authors also propose a phenomenological model based on this valence-state change which successfully accounts for all experimentally observed features. A brief summary of the impact of In doping into the polar semiconductor GeTe can be found in Sec. S1 of the Supplemental Material (SM) [26].

The motivation of the present work is to test and further elucidate the valence-skipping scenario proposed in the literature by a different and complementary approach. Here we present a comprehensive ^{115}In -NMR study on polycrystalline samples $\text{Ge}_{1-x}\text{In}_x\text{Te}$ with $0 < x \leq 1$. We find a steplike change of the nuclear quadrupole resonance (NQR) frequency ν_z when traversing $x \sim 0.4$, which coincides with a shift of the peak position in PES data on this system reported in Ref. [21]. Concomitantly, the nuclear spin-spin relaxation rate $1/T_2$ is strongly enhanced which is explained as indicative of the anticipated change in the In valence state. Based on these data, we propose a Ruderman-Kittel-Kasuya-Yosida (RKKY) type interaction model among the In nuclear spins through the conduction electrons at E_F which accounts for the observed changes in $1/T_2$. The most important result of this

*Contact author: yihara@phys.sci.hokudai.ac.jp†Contact author: markus.kriener@riken.jp

work is that $1/T_2$ and T_c exhibit a strikingly similar x dependence underlining the sensitivity and significance of $1/T_2$ measurements in valence-skipping materials. Moreover, this observation implies a close relationship between these two quantities and suggests that in $\text{Ge}_{1-x}\text{In}_x\text{Te}$ the valence degree of freedom may be indeed one driving force for the observed enhancement of the superconducting T_c with x .

The $\text{Ge}_{1-x}\text{In}_x\text{Te}$ batches were synthesized by conventional melt growth of stoichiometric mixtures of GeTe and InTe in evacuated quartz glass tubes. These were fired for 48–72 h at 950 °C and then quenched into water. For the batch with $x = 0.08$, x-ray diffraction (XRD) data confirmed the rhombohedral α -GeTe structure (space group $R3m$). For all other batches with $0.25 \leq x \leq 1$, XRD data of the obtained material indicates traces of the ambient-condition tetragonal InTe structure whose volume fraction quickly increases with x . To obtain superconducting cubic material, approximately 400 mg of each prereacted batch were treated in a second growth step in which a high-pressure synthesis method was employed (5 GPa, 600–1300 °C), cf. Ref. [21] for the details. The unit-cell volume shown in Fig. 1(b) was extracted from the XRD data taken on each final batch. We note that the lifetime of the metastable cubic structure is more than one year for samples containing Ge and In [21] and several months for pristine InTe [27]. To ensure the superconductivity, the T_c value for $x = 1$ was confirmed before and after the NMR experiment.

On selected batches the chemical composition was checked by energy-dispersive x-ray analysis. It was found that the actual In concentration fits to the nominal one with the difference between them slightly increasing for $x \rightarrow 1$; cf. the discussion in Ref. [21]. In the present work, the nominal composition is used when referring to a sample.

The superconductivity of the batches with $0.25 \leq x \leq 1$ was confirmed by temperature T dependent magnetization $M(T)$ measurements in a Quantum Design magnetic property measurement system (MPMS3) equipped with a ^3He refrigerator on samples cut into a well-defined geometry. Each sample was cooled down in zero magnetic field to the base temperature and $M(T)$ subsequently measured upon increasing temperature in an applied magnetic field $B = 1$ mT. The linear part of the magnetization below the transition was extrapolated and its intercept with the temperature axis defined as the superconducting T_c . The obtained T_c values fit well to the published data in Ref. [21].

The field-sweep NMR spectra were obtained by recording the fast-Fourier-transformed NMR intensity during magnetic field ($\mu_0 H$) sweeps. The NMR frequency was fixed to 41.51 MHz, which corresponds to the reference field $\mu_0 H_{\text{ref}} \approx 4.4$ T [28]. For the spin-echo pulse sequence, we utilized a shaped pulse to uniformly irradiate the radio-frequency field within the specified bandwidth of 400 kHz. [29] The measurement procedure of the spin-spin relaxation rate $1/T_2$ is described in detail in Sec. S4 in the SM [26].

Figure 1(a) summarizes ^{115}In -NMR spectra of $\text{Ge}_{1-x}\text{In}_x\text{Te}$. All spectra consist of a central peak accompanied by broad tails on either side. The peak position evolves almost linearly with x , shifting toward slightly smaller fields as indicated by triangle symbols in Fig. 1(a).

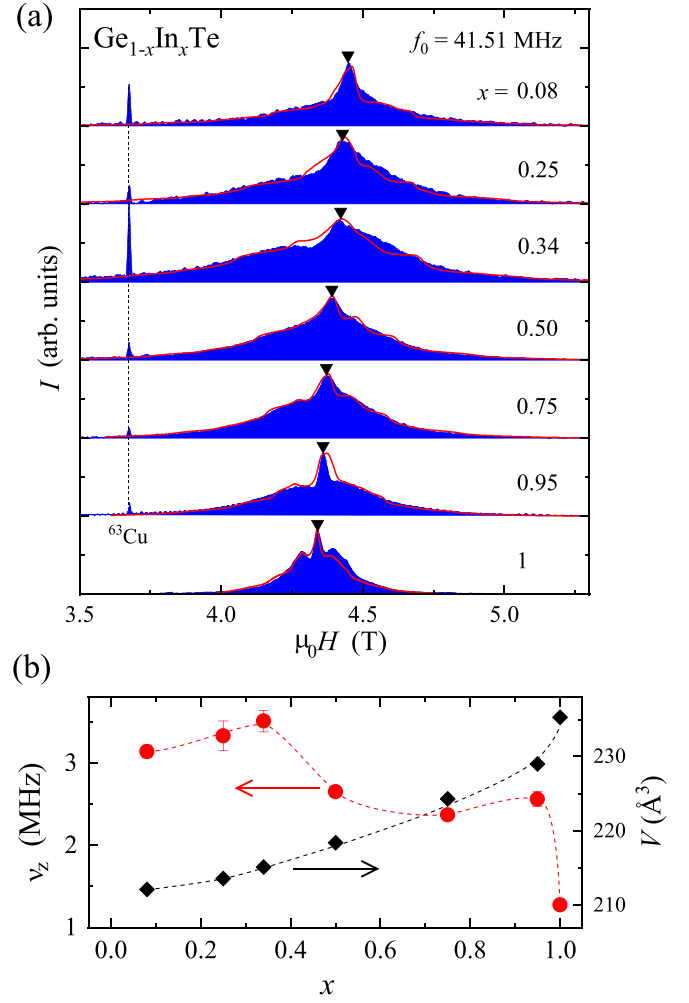


FIG. 1. (a) ^{115}In -NMR spectra of $\text{Ge}_{1-x}\text{In}_x\text{Te}$ on different samples taken at $T = 4.2$ K ($0.08 \leq x \leq 0.95$) and at $T = 1.6$ K ($x = 1$). We note that the spectral shape does not exhibit any temperature dependence below 10 K. The spectra are vertically shifted for clarity. The black triangles highlight the central peak positions and red curves are fits of the spectral shapes; see text. The peaks at $\mu_0 H \sim 3.7$ T in the data for $x < 1$ are due to the Cu coil used in the NMR experiments. In the measurement of $x = 1$ the narrower spectrum allowed to limit the field range to $3.8 \leq \mu_0 H \leq 5.0$ T explaining the absence of the Cu peak. (b) Extracted nuclear quadrupole resonance frequencies $\nu_z(x)$ (red filled circles; left coordinate axis) and unit cell volume V (black diamonds; right axis). The dashed lines are guides to the eyes.

These NMR spectral shapes are understood as powder patterns for the ^{115}In nuclear spin $I = 9/2$ with allowing some asymmetry as follows: The nuclear spin Hamiltonian is given by the sum of the Zeeman and the electric quadrupolar interactions [30],

$$\mathcal{H} = -\gamma \hbar (1+K) \mu_0 \mathbf{H}_0 \cdot \mathbf{I} + \frac{\nu_z}{6} \left[(3I_z^2 - I^2) + \frac{1}{2} \eta (I_+^2 + I_-^2) \right].$$

Here, γ is the gyromagnetic ratio [28], K is the Knight shift along the given orientation of the external field $\mu_0 \mathbf{H}_0$, η represents the asymmetry of the electric field gradient (EFG) tensor around each In nuclear spin $\mathbf{I}$, and $\hbar$ denotes the reduced

Planck constant. The overall spectrum width is determined by the electric quadrupolar interaction, namely the NQR frequency ν_z . This frequency is proportional to the largest EFG found along one of the three principal axes of the EFG tensor [30]. The ^{115}In -NMR spectra [Fig. 1(a)] exhibit a slight broadening at intermediate doping, suggesting a systematic variation of ν_z as a function of x . To further analyze this, we fitted each powder pattern by optimizing the parameters ν_z , η , and K . The results are shown as red curves in Fig. 1(a), describing the data reasonably well; cf. also Sec. S2 in the SM [26]. We note that the finite $\eta = 0.3 \pm 0.1$ deduced from our fittings exhibits only a weak x dependence.

Figure 1(b) (left axis) shows ν_z extracted for each x . Initially, ν_z increases with x . The largest value of ν_z is found for the sample with $x = 0.34$. Toward $x = 0.5$, ν_z is strongly suppressed and remains roughly constant above except for $x = 1$, for which another abrupt decrease of ν_z is observed. To understand the x dependence of ν_z , one has to keep in mind that the EFG at the In sites is mainly determined by two different factors: (i) the crystal-lattice contributions from the ions surrounding an In site and (ii) the contributions due to interactions between charge carriers and nuclear In spins. The former, which should be zero when an In ion experiences perfect cubic symmetry, is caused by local distortions breaking the cubic symmetry around an In dopant when replacing a Ge ion. Hence, the In ions themselves create the EFG due to their different point charges as compared to Ge. In the present case, this contribution is expected to lead to a monotonic suppression of ν_z with x because the crystal lattice of $\text{Ge}_{1-x}\text{In}_x\text{Te}$ expands monotonically as a function of x up to $x = 1$, as shown in Fig. 1(b) (right axis): The distance between neighboring ions increases, which in turn weakens the lattice EFGs. For pristine InTe with an ideal cubic structure, contributions from the lattice EFG are expected to vanish. Hence, the observed nonmonotonic x dependence of ν_z and its finite value for $x = 1$ imply that the interactions between the nuclear spins and the charge carriers produce a sizable contribution to the EFG, and thus dominate $\nu_z(x)$.

Interestingly, the strong suppression of $\nu_z(x)$ across $x \geq 0.34$ coincides with a change of the peak energy in In- $3d_{5/2}$ core-level PES data reported in Ref. [21]. Therein, this change was attributed to a crossover in the majority valence state of the In ions from trivalent to monovalent, suggesting that the suppression in $\nu_z(x)$ has the same origin. However, the spectroscopic approach usually yields intrinsically broad spectra, complicating the distinction of the involved mixed valence states. Therefore, we performed complementary nuclear spin-spin relaxation rate $1/T_2$ measurements to probe the effect of valence mixing, which are summarized in Fig. 2. The relaxation time T_2 is the typical timescale on which nuclear spins lose their coherence in the interaction with their local environment. Experimentally $1/T_2$ was determined by recording the spin-echo signal intensity $\mathcal{M}$ as a function of the separation time τ between two spin-echo pulses as sketched in Fig. 2(a) [31]. Then the Lorentzian function $\mathcal{M}(\tau) = M_0 \exp(-\tau/T_2)$ was fitted to each data set with the equilibrium magnetization M_0 of the undisturbed nuclear spin system; cf. [30] and Secs. S3 and S4 in the SM [26]. The results are shown as grey dashed lines in Fig. 2(b), which

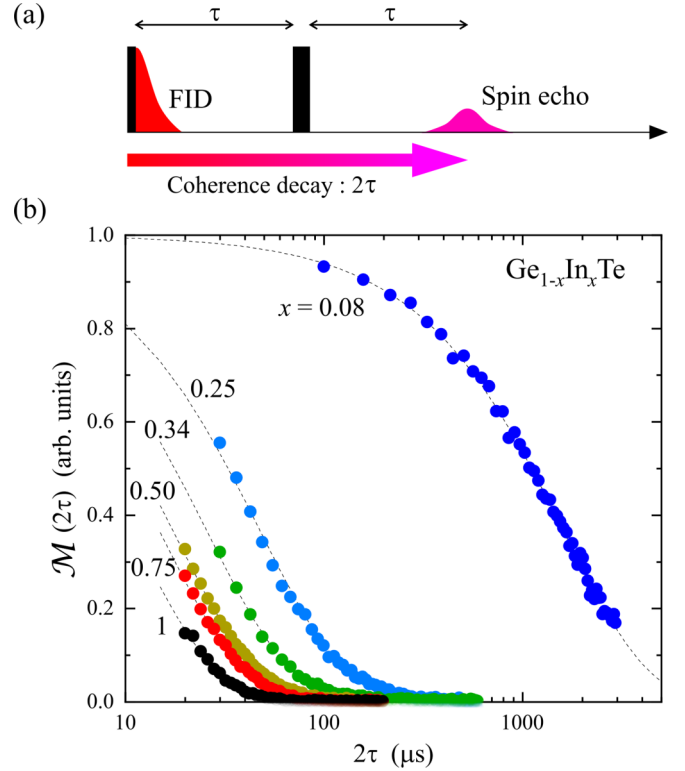


FIG. 2. (a) Sketch of spin-echo measurements and definition of the spin-echo pulse separation time τ . The free-induction decay (FID) signal observed after the first pulse disappears immediately and the spin-echo signal appears at a time τ after the second pulse. (b) Spin-echo intensity $\mathcal{M}$ for $\text{Ge}_{1-x}\text{In}_x\text{Te}$ with $0.08 \leq x \leq 1$ measured as a function of τ . Grey dotted lines are Lorentzian fits to the data. The decay curves were measured at 4.2 K for $0.08 \leq x \leq 0.75$ and at 1.6 K for $x = 1$. The decay curve for $x = 0.95$ overlaps with that for $x = 0.75$ and is not shown here for clarity.

reproduce the experimental data well. The extracted x dependence of $1/T_2$ is replotted in Fig. 3(a). The lowest-doped sample $x = 0.08$ exhibits an extremely slow relaxation. Upon increasing x , $1/T_2$ is drastically enhanced for $x \leq 0.34$ and tends to saturate toward $x = 0.95$. For $x = 1$, a jump-like enhancement is observed. Apparently, these features coincide with the suppression of $\nu_z(x)$ across $x = 0.34$, the approximately constant behavior up to $x = 0.95$, and the subsequent strong suppression for $x = 1$; cf. Fig. 1(b).

Moreover, when comparing $1/T_2$ shown in Fig. 3(a) with the superconducting T_c displayed in Fig. 3(b), a strikingly similar x dependence of both quantities becomes apparent, suggesting a close correlation between them, which will be discussed later.

To explain and contextualize the observed x dependences of ν_z and $1/T_2$, one has to keep in mind that the decay rate $1/T_2$ is determined by the interaction between neighboring In nuclear spins. The initially very small value of $1/T_2$ and its strong increase toward intermediate x cannot be explained by any simple dipole-dipole coupling, which is purely a function of the In-In distance and, hence, is expected to vary smoothly with x [30]. Therefore, another mechanism must be at work for which we propose an RKKY-type scenario based on the anticipated valence-state change with x as illustrated in Fig. 4.

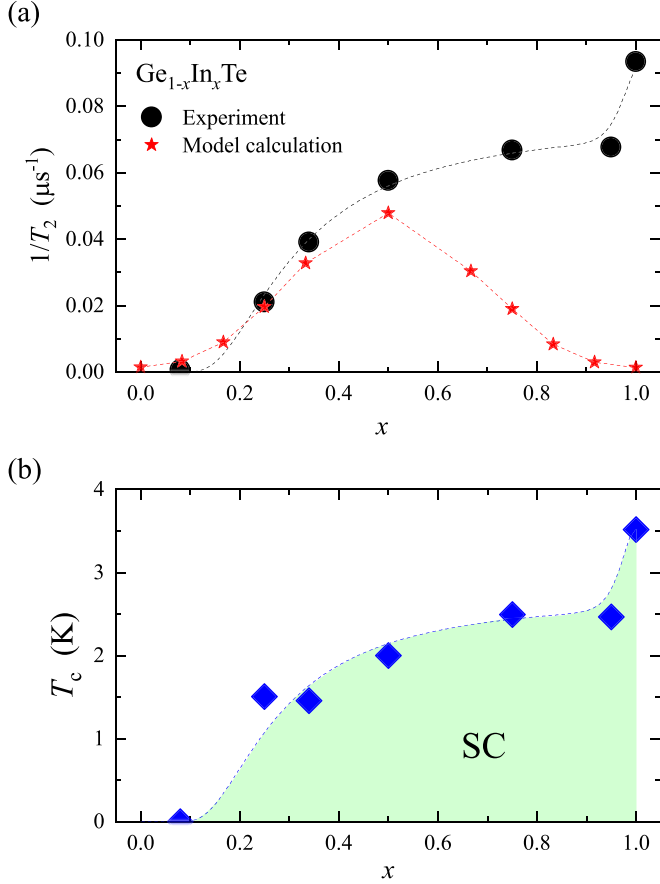


FIG. 3. (a) In concentration x dependence of $1/T_2$ deduced from the spin-echo decay curves (black filled circles) along with the results of model calculations (red stars); see text for details. (b) Evolution of the superconducting transition temperature T_c [21]. The superconducting phase (SC) emerges with x and increases concomitantly with a change of the majority In valence state from In^{3+} to In^{1+} ; see text for details. The dashed lines in both figures are guides to the eyes.

Before discussing the details, we note that in an RKKY-type interaction the conduction electrons at E_F mediate the scalar interaction between two nuclear spins i and j described by the Hamiltonian $\mathcal{H}_{\text{RKKY}} = A_{ij} \mathbf{I}_i \cdot \mathbf{I}_j$. The coupling constant A_{ij} is determined by the hyperfine coupling strength between the conduction electrons and the In nuclear spins, the effective mass of the electrons, and the Fermi wave number of $\text{Ge}_{1-x}\text{In}_x\text{Te}$. Hence, A_{ij} is a function of the charge carrier concentration n at E_F and, thus, the interaction between neighboring In nuclei strongly depends on n . If $\mathcal{H}_{\text{RKKY}}$ and the nuclear spin operator $\mathbf{I}$ commute, the RKKY interaction does not destroy the quantum state of the nuclear spins. This is the case if two interacting nuclear spins $\mathbf{I}_i$ and $\mathbf{I}_j$ are experiencing the same uniform local electronic state as it is the case when both nuclear spins belong to In ions with the same valence state. This will not affect $1/T_2$. However, the commutator $[\mathcal{H}_{\text{RKKY}}, \mathbf{I}]$ becomes finite when these interacting nuclear spins are in different electronic environments, i.e., experience different EFGs, which results in a shift in the resonance condition. Such a situation is realized when the interacting nuclear spins belong to In dopants with different valence states and will significantly enhance $1/T_2$ [32].

Additional remarks concerning this RKKY-type interaction between nuclear spins can be found in Sec. S5 in the SM [26].

Figure 4(a) sketches the situation for small x : Only a few In^{3+} ions are embedded in the Ge-dominated background. Since these are distributed homogeneously, they are too far away from each other and the carrier concentration [21] is too small to allow for any sizable RKKY-like interaction among their nuclear spins. Hence, the respective coupling constant A_{TT} (“T” = trivalent) is small. When performing a spin-echo measurement at the In sites, each In nuclear spin resonates almost independently. As a result, $1/T_2 \rightarrow 0$, in agreement with our experimental observation for $x = 0.08$.

This changes upon increasing x as shown in Fig. 4(b), which sketches the situation for intermediate x : The number of In nuclei and n are larger [21], which enhances the coupling constant A_{ij} and, hence, the RKKY interaction. Moreover, now there are also In^{1+} ions present resulting in two additional interaction paths with coupling constants A_{MM} and A_{MT} (“M” = monovalent). Since the nuclear spins of In^{3+} ($\mathbf{I}_T$) and In^{1+} ($\mathbf{I}_M$) experience a different electrical environment, as also reflected in the strong change of v_z with x , the Hamiltonian $\mathcal{H}_{\text{RKKY}}$ does not commute any more with $\mathbf{I}_T$ and $\mathbf{I}_M$. This leads to a faster decay in the spin-echo intensity which perfectly describes what is seen in Fig. 3(a): $1/T_2$ is strongly enhanced toward intermediate x .

Upon further increasing x , more and more cation lattice sites are occupied by In^{1+} ions as illustrated in Fig. 4(c). This provides a strong RKKY-type correlation among them mediated by a large number of conduction electrons at the Fermi level. However, if all In ions were in their monovalent state at large x , $\mathcal{H}_{\text{RKKY}}$ would commute again with the nuclear spin operators $\mathbf{I}_M$ because all In nuclear spins would feel the same local electronic environment. Hence, in spite of the large prefactor A_{MM} , $1/T_2$ should decrease toward large x , in contradiction to the experimental result. To simulate this, we performed model calculations for $1/T_2$ based on the following scenario: At small x , there are only In^{3+} ions. Upon increasing x , also In^{1+} ions are present and the ratio of the populations of In^{3+} and In^{1+} changes from large to small as a function of x ending for $x = 1$ with In^{1+} only; cf. also Sec. S6 in the SM [26]. The results are shown in Fig. 3(a) along with the experimental $1/T_2(x)$. As expected, the simulation yields a domelike x dependence, indicating that the decay of the nuclear-spin coherence is accelerated by the admixture of In^{3+} and In^{1+} peaking at intermediate doping. Apparently, this does not agree with our experimental observation that $1/T_2$ remains large at large x . This failure of the model calculations can only be explained if there are still sufficiently many In^{3+} ions present for $x \rightarrow 1$, either statically or due to valence fluctuations, to allow for interactions with the In^{1+} sites resulting in a large $1/T_2$. In Sec. S7 in the SM [26], a rough estimation of the lower border for the required number of remaining In^{3+} ions is given.

The final question to address is why $x = 1$ is such an outlier: While both quantities $v_z(x)$ and $1/T_2(x)$ are roughly constant for $x \rightarrow 1$, in pristine InTe the former is significantly suppressed and the latter strongly enhanced. This apparent impact on $v_z(x)$ and $1/T_2(x)$ when only slightly changing the In content from $x = 0.95$ to $x = 1$ could indicate that the crystal-lattice contributions to the EFG are different in

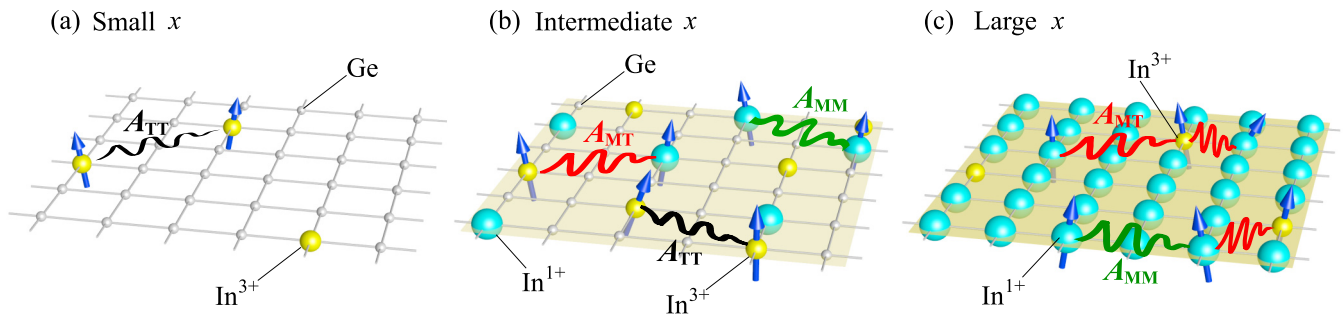


FIG. 4. Sketch of the situation in a (Ge,In) sublayer in $\text{Ge}_{1-x}\text{In}_x\text{Te}$ for (a) small, (b) intermediate, and (c) large x . The grey, yellow, and blue balls represent Ge, In^{3+} , and In^{1+} , respectively. The background yellow shade depicts the concentration of the charge carriers, which increases as a function of x ; cf. Sec. S1 in the SM [26]. The In nuclear spins (blue arrows) are shown only on selected In sites for a better visibility. Exchange interactions between different nuclear spins are indicated by black, green, and red bands and labeled A_{TT} ($\text{In}^{3+} - \text{In}^{3+}$; “T” = trivalent), A_{MM} ($\text{In}^{1+} - \text{In}^{1+}$; “M” = monovalent), and A_{MT} ($\text{In}^{1+} - \text{In}^{3+}$). At small x , only A_{TT} exchange is present because of the absence of In^{1+} . This changes upon increasing x , leading to the appearance of the additional exchange interactions A_{MT} and A_{MM} . Finally, at large x , the impact of the A_{TT} exchange vanishes because of the more and more increasing distances between the remaining In^{3+} ions. See text for details.

$\text{Ge}_{1-x}\text{In}_x\text{Te}$ for $x < 1$ and $x = 1$. While they are most likely negligible for $x < 1$, as argued above, this may change when divalent Ge is very diluted or completely absent. The larger $1/T_2$ for $x = 1$ also indicates that pure InTe is prone to possibly enhanced valence fluctuations as compared to $x < 1$. Starting with InTe, Ge may introduce local lattice distortions which relax the frustration caused by valence-skipping In, leading to a longer decay time for $x < 1$ as compared to pristine InTe.

Remarkably, the observed x dependence of the spin-echo relaxation rate $1/T_2$ [Fig. 3(a)] almost perfectly resembles the x dependence of the superconducting T_c [Fig. 3(b) [21]] in the whole solid solution $\text{Ge}_{1-x}\text{In}_x\text{Te}$. This suggests an inherent coupling between both quantities and, hence, a close correlation between the valence-skipping feature of In and the evolution of the superconductivity in $\text{Ge}_{1-x}\text{In}_x\text{Te}$. Especially the additional strong enhancement of both when going from $x = 0.95$ to $x = 1$ possibly indicates that enhanced valence fluctuations are indeed supportive of the superconductivity as theoretically suggested [1], which is a tempting starting point for future studies on pristine InTe [24].

This work reports a comprehensive ^{115}In -NMR study on $\text{Ge}_{1-x}\text{In}_x\text{Te}$. We find a strong enhancement of the spin-spin relaxation rate $1/T_2$ when traversing $x = 0.34$ and its

subsequent saturation. This is explained as indicating a change in the majority In valence state from trivalent to monovalent as a function of x . Concomitantly, we also observe a remarkably similar x dependence of $1/T_2$ and the superconducting transition temperature T_c . These findings point toward a scenario in which this valence-state change as a function of x in $\text{Ge}_{1-x}\text{In}_x\text{Te}$ and possibly enhanced valence fluctuations in InTe are beneficial for the superconductivity in this solid solution. Hence, this work provides strong indications that the valence-skipping feature of some elements can indeed be in favor of enhancing the superconducting pairing interaction as theoretically predicted.

The present work also demonstrates the high potential and power of approaching valence-state physics by means of spin-echo measurements, i.e., exploring electric properties of a solid with an essentially magnetic probe. This suggests employing this technique also for other materials in which the valence degree of freedom may play a crucial role.

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