Gallium and thallium NMR study of phase transitions and incommensurability in the layered semiconductor TlGaSe₂

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We report on the first NMR study of phase transitions and incommensurability in the layered semiconductor TlGaSe₂. ^{69,71}Ga and ^{205}Tl NMR data from a powder sample show phase transitions at 118, 108 and around 69 K. The ^{69}Ga and ^{71}Ga spin-lattice relaxation times T_1 are short and nearly temperature independent in the temperature range 118 to 108 K, which is characteristic of an incommensurate state. The nuclear magnetization recovery in this temperature range can be fit by two components having different time constants. The ratio of the amplitudes of the components varies with temperature. Such behavior is consistent with the coexistence in this temperature range of two different macroscopic domains, such that one of the domains becomes energetically favored on cooling. The phase transition into a ferroelectric phase at 108 K appears to be accompanied by a displacement of Tl atoms.

I. INTRODUCTION

Ternary chalcogenide TlGaSe₂ is a quasi-two-dimensional compound whose structure consists of layers formed by corner-linked GaSe₄ tetrahedra and Tl^{1+} ions located on straight lines between the layers[1–3] (Fig. 1). It belongs to the TlMX_2 (M=In,Ga, X=S,Se,Te) family that is of interest due to its low dimensionality, semiconducting and photoconducting properties, negative differential resistance regions in the I-V characteristics, memory effects and second harmonic optical generation.[4–11] Furthermore, TlGaSe₂ exhibits successive phase transitions and has an intermediate incommensurate (IC) phase.[12–15] Phase transition temperatures T_c and T_i, reported by different authors, were found between 107–110 K (T_c) and 117–120 K (T_i), respectively. Here T_i corresponds to a high temperature normal-incommensurate transition, and T_c to a low temperature "lock-in" transition to a lower temperature commensurate (C) phase which is thought to extend from 108 K down to 12 K,[15,16] even though a detailed low temperature study of the C phase has not yet been performed. The phase transition at T_c has been reported to be first order, while that at T_i is second order.[15,16] Dielectric measurements show that the compound is ferroelectric below T_c, while the phase above T_i is paraelectric.[16] A submillimeter dielectric spectroscopy study by Volkov *et al.*[12] has shown that TlGaSe₂ exhibits soft mode behavior. Moreover, Volkov *et al.*[13] reported that in some TlGaSe₂ samples the soft mode splits into two components, each showing different behavior.

X-ray diffraction measurements in a single crystal of TlGaSe₂ (Ref. 15) show that the IC structure between 117 and 110 K is characterized by a modulation wave having a wave vector $(\delta,\delta,1/4)$ where $\delta\approx0.02$ reciprocal lattice units. Reduction of the temperature from 117 to 110 K yields some decrease in δ, until it jumps discontinuously to zero at T_c=110 K to produce a commensurate phase. The scattering

from the low temperature commensurate ferroelectric phase indicates a quadrupling of the unit cell along the c axis compared to that of the high temperature phase. This phase was assigned to the space group Cc.[16] A recent single crystal neutron scattering study of TlGaSe₂ by Kashida *et al.*[17] showed the existence of an IC state between
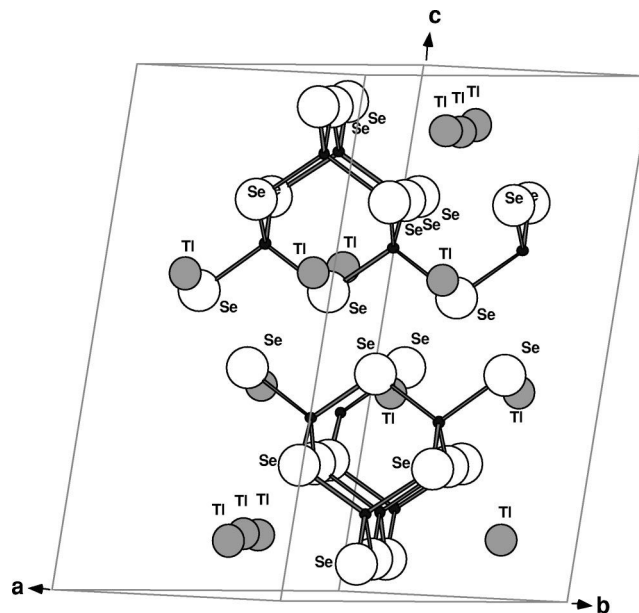

FIG. 1. Structure of TlGaSe₂ comprises layers in the a,b plane. The layers are built from large linked Ga₄Se₁₀ tetrahedra consisting of four corner-linked GaSe₄ tetrahedra and kept together by Tl^{1+} ions that are located between layers on straight lines along $[1,1,0]$ and $[1,-1,0]$ directions (at different height along c axis). The structure belongs to monoclinic symmetry, the space group is $C2/c-C_{2h}^6$, a=10.772 Å, b=10.771 Å, and c=15.636 Å, β=100.6°, Z=16 (Refs. 2 and 3). Ga atoms are shown by small filled circles.

107 and 118 K with a modulation wave vector $(\delta,0,1/4)$, where $\delta=0.04$. In the low temperature phase $(T<107$ K), the satellite reflections appear at the commensurate position $q_c=(0,0,\pm0.25)$.[17]

Dielectric measurements of Allakhverdiev *et al.*[18] and specific heat measurements of Mamedov *et al.*[19] have shown the existence of two more phase transitions—at 65 and 252 K.

Nuclear magnetic resonance (NMR) is a unique technique that has been widely used[20–22] to study IC systems, since temperature-dependent NMR spectra and spin-lattice relaxation measurements readily reflect the spatial variation of the incommensurate structure and modulation wave dynamics in an IC phase.

In the present paper we report on the first NMR study of incommensurability and phase transitions in the layered semiconductor $TlGaSe_2$. In particular, we provide experimental data that confirm the existence of the IC phase in the temperature range 108 to 118 K and, furthermore, we have shown that this phase consists of two distinct domains that are probably interspersed through the structure.

II. EXPERIMENTAL FEATURES

Two powder $TlGaSe_2$ samples prepared at the Middle East Technical University and Niigata University were used. ^{69}Ga, ^{71}Ga, and ^{205}Tl NMR measurements of powder $TlGaSe_2$ were performed using a Tecmag pulse NMR spectrometer, an Oxford Instruments cryostat, and an Oxford superconducting magnet (external magnetic field $B_0=8.0196$ T). ^{69}Ga and ^{71}Ga NMR spectra and spin-lattice relaxation times (T_1) were measured at their respective resonance frequencies 81.95 and 104.133 MHz in the temperature range 69–295 K. The spectra were obtained from the Hahn echo $(\pi/2\text{-}\tau\text{-}\pi)$ pulse sequence with phase cycling. The T_1 of each isotope was measured by means of a saturation comb sequence. The duration of the $\pi/2$ pulse was 1.8 to 2 μs for ^{71}Ga, 2.1 to 2.3 μs for ^{69}Ga, and 5.2 to 5.5 μs for ^{205}Tl depending on temperature. The ^{205}Tl spin-lattice relaxation time T_1 was also measured by means of the saturation comb sequence in the temperature range 94–290 K.

The NMR spectra and relaxation time behavior were observed to be similar in both $TlGaSe_2$ samples.

III. RESULTS AND DISCUSSION

A. ^{69}Ga and ^{71}Ga spin-lattice relaxation

The results of gallium spin lattice relaxation time measurements are shown in Figs. 2 and 3. A comparison of the spin-lattice relaxation times for the two gallium isotopes shows that the ratio $T_1(^{71}Ga)/T_1(^{69}Ga)$ is around 2.7. [For instance, at ambient temperature $T_1(^{71}Ga)=148$ ms, while $T_1(^{69}Ga)=55.4$ ms.] This value for the $T_1(^{71}Ga)/T_1(^{69}Ga)$ ratio is close to $[Q(^{69}Ga)/Q(^{71}Ga)]^2=2.51$, where Q is the nuclear quadrupole moment. This result is in accord with the well-known formula for quadrupolar relaxation[23] which assumes that the coupling of lattice vibrations with the quad-
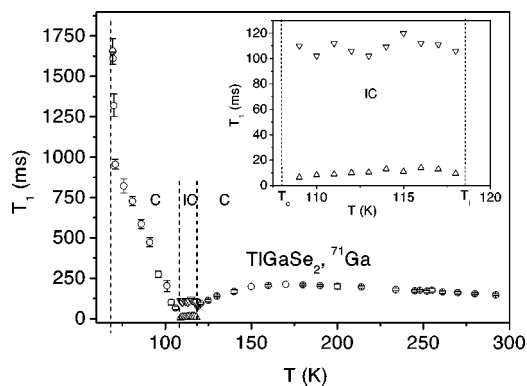

FIG. 2. Temperature dependence of ^{71}Ga spin-lattice relaxation time in $TlGaSe_2$. In the inset, the relaxation times resulting from the two-exponential fit [Eq. (1)] are shown. Vertical dashed lines show the phase transition temperatures.

rupole moment is the main relaxation mechanism for nuclear spins $I>1/2$, as is usually the case.

In the high temperature paraelectric phase, a weak increase in T_1 on cooling from 300 to 170 K is observed. Such behavior is known to be caused by torsional vibrations that cause fluctuations of the electric field gradient (EFG).[24] The spin-lattice relaxation rate $1/T_1$ is a measure of the spectral density of these fluctuations at the Larmor frequency. As shown in Figs. 2 and 3, T_1 reaches its maximum at around 170 K and then decreases on further cooling. Such behavior indicates the presence of an extra relaxation mechanism. This decrease in T_1 likely reflects the softening of the critical fluctuations (soft mode) in the high-temperature paraelectric phase on approaching the phase transition at T_i. In $TlGaSe_2$, such soft mode behavior was discovered by Volkov *et al.*[12,13] by means of submillimeter dielectric spectroscopy measurements in a wide temperature range, from room temperature down to the phase transition temperature. This mode may be represented by vibrations of the $GaSe_4$ tetrahedra with one of their axes in the Ga-Se layers. Such a mechanism may result in a slight averaging of the EFG, yielding the line narrowing on cooling from 300 to 118 K mentioned in the next section. We note that heat capacity measurements[16] show not only
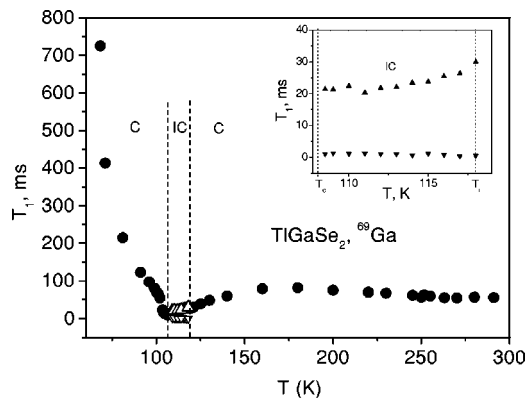

FIG. 3. Temperature dependence of ^{69}Ga spin-lattice relaxation time in $TlGaSe_2$. In the inset, the relaxation times resulting from the two-exponential fit [Eq. (1)] are shown. Vertical dashed lines show the phase transition temperatures.
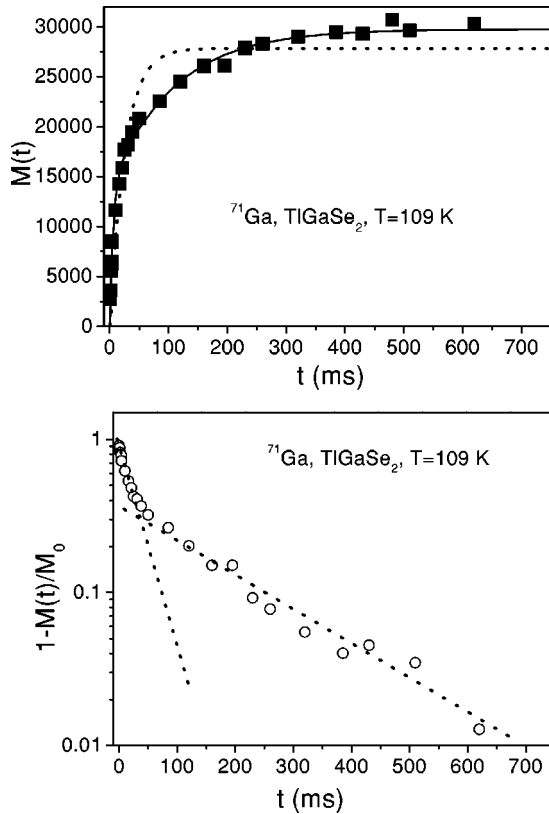
FIG. 4. ^{71}Ga magnetization recovery in the linear (top) and half-logarithmic (bottom) scales. Dashed and solid lines on the top figure show single and two-exponential fit, respectively.

FIG. 5. Temperature dependence of the amplitude ratio in Eq. (1) for ^{69}Ga. M_1 and M_2 belong to the fast and slow components, respectively.

two peaks at around 110 and 120 K but also a deviation from the regular behavior of C_p on cooling. This deviation starts around 140 K, thereby correlating with the NMR data.

The phase transition at $T_i = 118$ K is not accompanied by drastic changes in T_1. The absence of a discontinuity is typical of a second-order phase transition. However, even though the ^{69,71}Ga nuclear magnetization recovery is exponential in the high temperature phase, it cannot be fit by a single exponential in the temperature range from 108 to 118 K. In this temperature range, the magnetization recovery is well fit by a superposition of two exponentials (Fig. 4):

$$M(t) = M_1(0) \times [1 - \exp(-t/T_{11})] + M_2(0)$$
$$\times [1 - \exp(-t/T_{12})]. \tag{1}$$

Both T_{11} and T_{12} obtained from this fit are nearly temperature independent in the range from 118 to 108 K (Figs. 2 and 3), which is characteristic of the incommensurate state. The ratio of the amplitudes of the magnetization components in Eq. (1) is a function of temperature (Fig. 5) with the slow component (M_2) increasing on heating. We note that both samples under study show similar behavior, as expected. This behavior suggests the coexistence of two types of phases (or domains) in this temperature region. One of the phases (or domains), showing a faster relaxation rate, presumably becomes energetically preferred on cooling and then increases its size at the expense of the other phase. This model
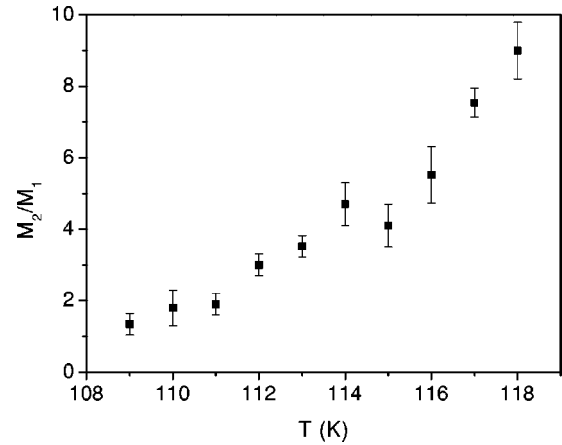
explains the observed two-exponential behavior and temperature variation of the M_2/M_1 ratio and therefore is consistent with the NMR data. We note that specific heat measurements[19] in TlGaSe$_2$ show irregular behavior in the temperature dependence of C_p at $108-118$ K that may reflect the aforementioned phase redistribution.

In the low temperature commensurate ferroelectric phase ($T < 108$ K), a strong increase in T_1 with cooling was observed. Such behavior is due to the change in the phason spectrum and disappearance of the soft mode fluctuations below the phase transition into the C phase. A sudden change in spin-lattice relaxation time observed on approaching $T \sim 69$ K correlates with the behavior of the linewidth (see the next section), and is attributed to the next low temperature phase transition, which was reported by Allakhverdiev *et al.* to occur at around 65 K.[18] Our measurements were carried out in the temperature range $69-292$ K—and, thus, this phase transition is below the lower limit of the temperature range of our study.

B. ^{69}Ga and ^{71}Ga NMR spectra

Both ^{69}Ga and ^{71}Ga are quadrupolar nuclei having $I = 3/2$. The ^{69}Ga and ^{71}Ga NMR spectra of powdered TlGaSe$_2$ for the $\frac{1}{2} \rightarrow -\frac{1}{2}$ transition are given for different temperatures in Figs. 6 and 7. In a powder the shape of such quadrupolar perturbed NMR lines is determined by second order quadrupole coupling effects, and shows several singularities.[25,26] Their relative positions depend on the $(e^2qQ/h)^2/\omega_L$ ratio, where ω_L is the Larmor frequency, e^2qQ/h is the quadrupole coupling constant, and q is the electric field gradient at the nuclear site. Note that a splitting is observed in the room temperature ^{69}Ga NMR spectrum (Fig. 6). A line shape analysis (see Fig. 8) yields the values 1.5 MHz for the quadrupole frequency $\nu_Q = 3e^2qQ/2hI(2I-1)$ and 0.5 for the asymmetry parameter η (with a precision of about 10%). However, the line splitting is not observed in the ^{71}Ga NMR spectra, which show slightly asymmetric lines at least down to 100 K. Since the ratio $Q(^{69}$Ga$)/Q(^{71}$Ga$) = 1.6$, the splitting in ^{69}Ga spectra
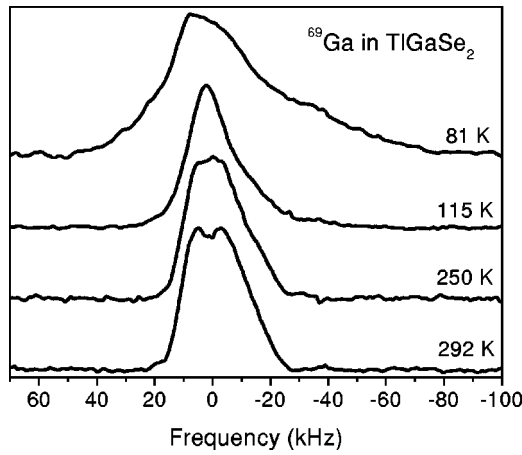
FIG. 6. ^{69}Ga NMR spectra of powder TlGaSe$_2$ at different temperatures ($\frac{1}{2} \rightarrow -\frac{1}{2}$ transition).

must be caused by a quadrupole interaction for ^{69}Ga that is larger than that for ^{71}Ga. The absence of the fine structure in the ^{71}Ga resonance means that in the magnetic field of 8.0196 T the quadrupole splitting cannot be larger than the broadening resulting from dipole-dipole interactions among nuclear spins and, from Tl-Ga indirect spin-spin interactions; the latter were shown to exceed the dipole-dipole by an order of magnitude.[27]

The temperature dependencies of the linewidth $\Delta\nu$ are shown in Figs. 9 and 10. The dependence for ^{71}Ga is different than that for ^{69}Ga. While the ^{71}Ga linewidth is nearly temperature independent from 295 to 140 K, the width of the ^{69}Ga resonance experiences some narrowing on cooling in this temperature range. Moreover, the splitting in the ^{69}Ga spectra is gradually decreased on cooling and is not seen below ~ 250 K. The absence of dramatic changes in the spectra and relaxation times (Sec. III A) suggests the absence of a phase transition in this temperature range. However, the ^{69}Ga NMR line narrowing with reduced temperature (Fig. 9) is unusual. The possible causes for this temperature dependence are a reduction of the quadrupole coupling constant e^2qQ/h (due to a reduction of the EFG), and/or an increase of the asymmetry parameter η. Similar effects have been
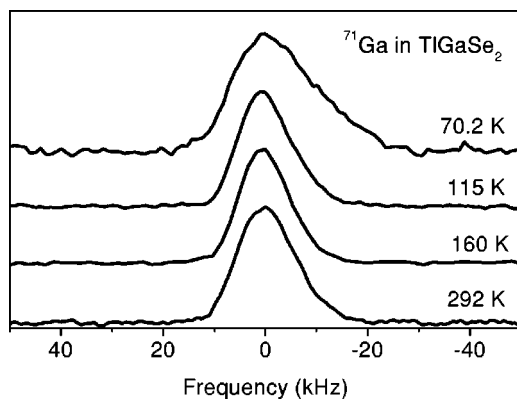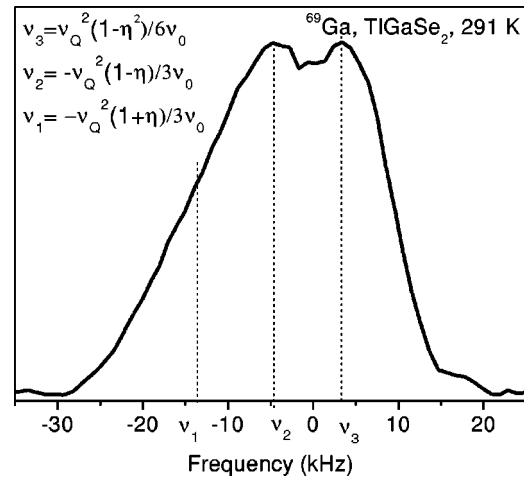

FIG. 8. Analysis of the room temperature ^{69}Ga NMR powder spectrum. All formulas are taken from Ref. 26. ν_1 position is found from the first derivative of the NMR line. For $\nu_3 = 3.4$ kHz, $\nu_2 = -4.6$ kHz, $\nu_1 = -13.7$ kHz, and $\nu_0 = 81.95$ MHz, one can evaluate $\nu_Q = 1.5$ MHz, $\eta = 0.5$.

reported in the temperature range 330 to 150 K.[28] Nevertheless, such effects are not seen in the ^{71}Ga spectra, in which the contribution of the quadrupolar coupling is not dominant and is smaller than that for ^{69}Ga, as mentioned above. This effect was discussed in the previous section.

The aforementioned ^{69}Ga NMR line narrowing on cooling stops at the phase transition temperature $T_i = 118$ K. Further cooling yields gradual line broadening that is characteristic of an IC phase and is caused by a quasicontinuous distribution of the electric field gradients. We note that the increase in $\Delta\nu$ is rather weak since the quadrupole splitting in the high magnetic field $B_0 = 8.0196$ T used in our experiment is masked by the broadening factors mentioned above. Therefore the line broadening between $T_c = 108$ K and $T_i = 118$ K is not seen for ^{71}Ga resonance in which the contribution of the quadrupolar coupling is not dominant. The lock-in phase transition into a commensurate phase at $T_c = 108$ K is accompanied by a sharp increase of the linewidth $\Delta\nu$, leading to a significant change in the linewidth behavior. Such behavior

FIG. 7. ^{71}Ga NMR spectra of powder TlGaSe$_2$ at different temperatures ($\frac{1}{2} \rightarrow -\frac{1}{2}$ transition).
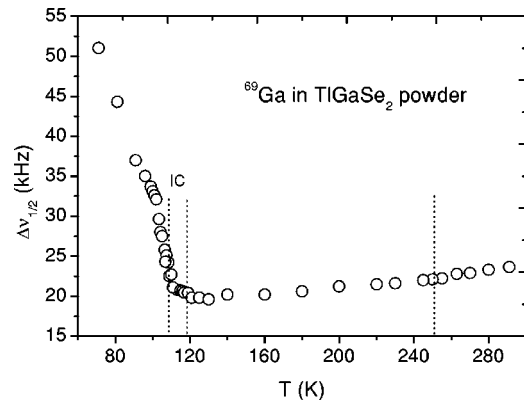

FIG. 9. Temperature dependence of ^{69}Ga NMR linewidth in TlGaSe$_2$. Vertical dashed lines show the phase transition temperatures.
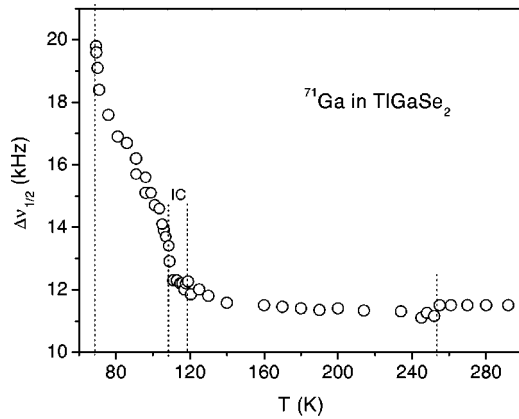
FIG. 10. Temperature dependence of ^{71}Ga NMR linewidth in TlGaSe$_2$. Vertical dashed lines show the phase transition temperatures.

is characteristic of a phase transition. Line broadening on further cooling becomes more noticeable in the low temperature phase (between 108 K and 69 K) for both ^{69}Ga and ^{71}Ga isotopes. This behavior is also typical of a system approaching a phase transition. A phase transition has been reported at 65 K,[18] but, unfortunately, this temperature is beyond the lower limit of the temperature range of our study.

C. Thallium NMR spectra and relaxation

Both ^{203}Tl and ^{205}Tl isotopes have spin $I=1/2$. Due to the absence of quadrupolar interactions, the ^{205}Tl nuclei show rather long spin-lattice relaxation times T_1 that increase from 8 to 40 s when the temperature is reduced from 290 K to 118 K (Fig. 11). Such behavior is typical for semiconductors in which the nuclear spin-lattice relaxation is caused by interaction of the nuclei with the conduction electrons and the relaxation rate $1/T_1$ varies with temperature as $(T)^{1/2}$.[29] We observed that the Tl magnetization recovery $M(t)$ is well
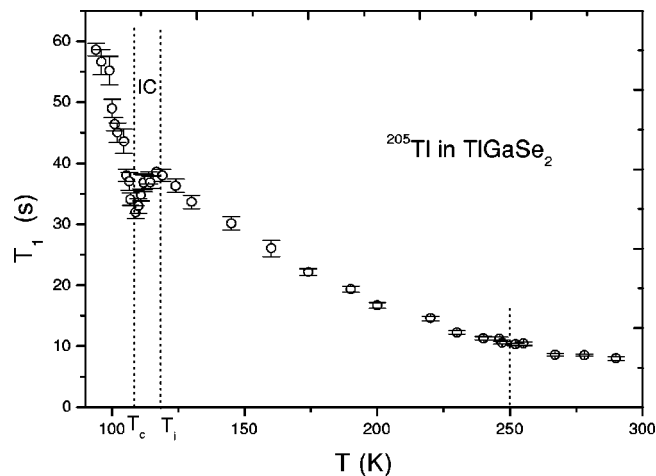

FIG. 11. Temperature dependence of ^{205}Tl spin-lattice relaxation time in TlGaSe$_2$ in magnetic field $B_0=8.0196$ T. Vertical dashed lines show the phase transition temperatures.

described by a single exponent in all temperature ranges under study, including the IC phase. For a spin $\frac{1}{2}$ nucleus like ^{205}Tl for which spin diffusion is rapid, it is probably not possible to distinguish the two exponential components from one another.

Phase transitions at 108 and 118 K are easily seen in the ^{205}Tl spin-lattice relaxation data (Fig. 11). The increase in T_1 stops at $T_i=118$ K and starts again below $T_c=108$ K in the low temperature phase. In the IC phase, the measured T_1 decreases on cooling. This decrease correlates well with the model of the coexistence of two phases mentioned previously. It may be explained by increase on cooling of the size of the phase showing faster relaxation at the expense of that showing slower relaxation. We note that the sharp increase in T_1 below 108 K correlates with x-ray data[15] that show at T_c a discontinuous jump to zero of the modulation wave vector parameter δ.

The phase transition around 252 K, seen in specific heat measurements,[19] is not evident in the Tl NMR results.

D. Discussion

As shown above, in the temperature region corresponding to the IC phase both ^{69}Ga and ^{71}Ga nuclear magnetization recoveries are well fit by a superposition of two exponentials. The ratio of the amplitudes of these magnetization components is temperature dependent, with the slow component increasing on heating. This behavior suggests the coexistence of two types of phases (or domains) in this temperature range. This conclusion is readily confirmed by ^{205}Tl relaxation data that show a decrease in T_1 on cooling, which is interpreted as an increase of the size of the phase showing faster relaxation at the expense of that showing slower relaxation. Owing to the narrowness of the temperature region (only 10 K) of phase coexistence, it was not possible to determine the nature of the domains (i.e., whether they are two different IC phases or one IC and one C phase).

An alternative possibility for explaining our data based on a single domain would assume that the two exponentials in the T_1 data arise from a combination of phason and amplitudon contributions. However, we will now show that this explanation is inconsistent with our observations of the temperature dependence of the magnetization ratio in Fig. 5. The NMR spectra of IC crystals are typically characterized by an inhomogeneous frequency distribution. The relaxation rate varies over this distribution (i.e., the NMR line), showing different values at the central part and on the edges of the line that are proportional to the phason and amplitudon spectral densities at the Larmor frequency, respectively.[30,31] In our case, a hard pulse excites the entire Ga NMR line. We note that (i) the amplitudon contribution corresponds to a longer T_1 than does the phason and (ii) the relaxation time assigned to amplitudons increases as the temperature is lowered, whereas the phason contribution to T_1 is temperature-independent.[21,31] This would suggest that the amplitude of the more slowly decaying component (and thus the ratio M_2/M_1) should increase as the temperature is lowered. However, such behavior is in direct contrast with our experimental observation that shows a reduction of M_2/M_1

on cooling in the IC phase (Fig. 5). Furthermore, in our powder measurements, the inhomogeneous effects due to the incommensurate modulation (including the spectral singularities) are probably masked by homogeneous line broadening interactions, such as indirect spin-spin and dipole-dipole couplings. Therefore, it is very unlikely that our two-component relaxation time data can be due to a combination of phason and amplitudon contributions from a single domain.

On the other hand, evolution of the incommensurate modulation from the plane wave limit to the multisoliton lattice very often occurs as the IC-C transition is approached from above. The results of relaxation measurements are often interpreted as an indication of the occurrence of a quasi-soliton lattice, in which the slow component is assigned to C-phase domains, while the fast component is assigned to the discommensurates (solitons). As T_c is approached from above, the gradual formation of such a lattice causes the phase solitons to become narrower so that almost the whole intensity of the spectrum concentrates in the C peaks. However, the M_2/M_1 transformation (Fig. 5) observed in our relaxation experiments shows on cooling an increase (rather than a decrease) of the fast component, which contrasts with the above scenario. The phase transition seems to be due to an instability that leads to a fragmentation into domains of C and IC (or maybe of two IC) phases. This fact correlates with irregular behavior in the temperature dependence of the specific heat at 108–118 K (Ref. 19) that may reflect the aforementioned phase redistribution. McMorrow *et al.*[15] were led to the same conclusion and speculated that the magnitudes of the modulation wave vector are characteristic of many IC-C transitions. Neutron diffraction data,[17] in principle, may also offer additional evidence for the coexistence of two phases in the range 108–118 K. In these experiments the satellite intensity was observed to increase on cooling, which may be interpreted as an increase in the relative amount of one of the phases.

Recent exciton spectroscopy and dielectric measurements in $TlGaSe_2$ (Ref. 32) show that the IC phase region may be considered as a coexistence of two spatially dispersed media with different dielectric constants and different behavior. This result agrees with our conclusion. Furthermore, Mikailov *et al.*[33] have reported a coexistence of type I and type II incommensurate structures in $TlInS_2$, which is isostructural to $TlGaSe_2$.

A full structural analysis of the low temperature phase has not been done. However, x-ray and neutron diffraction studies,[15–17] show small asymmetric positional shifts of the Tl^{1+} cations at the transition temperature destroying the inversion symmetry. The transition is found to be of displacive type and is accompanied by a change in symmetry from $C2/c$ to Cc. Our data show that ferroelectric phase transition at 108 K affects the Tl subsystem and thus are consistent with the conclusion that the transition is accompanied by a displacement of the Tl atoms. The asymmetric positional shifts of the Tl^{1+} cations may be caused by the formation at Tl^{1+} centers of directed, stereochemically active lone pairs due to the mixing of Tl $6p$ orbitals into the filled Tl $6s$ level. Such wave function hybridization was observed by one of us in Ref. 27. It was there shown that the indirect spin-spin couplings among Tl and Ga atoms via the intervening Se atoms result from the formation of weak interlayer Tl-Se-Tl and Tl-Se-Ga bonds. Such bonds allow Tl motions along the bonds, suggesting that the ferroelectric phase transition is accompanied by the Tl atoms displacements.

In summary, our ^{69,71}Ga and ^{205}Tl NMR data from a powder sample show phase transitions at 118, 108 and around 69 K. We conclude that our results not only confirm the incommensurability of the 108–118 K phase but more importantly demonstrate that this phase really consists of two coexisting domains (or phases). In addition, our thallium NMR observations at T_c are consistent with a phase transition that is characterized by the existence of Tl ion displacements which increase as the temperature is lowered in the ferroelectric phase.

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