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Markus Prinz-Zwick, T. Gimpel, Korbinian Geirhos, Somnath Ghara, C. Steinbrecht, Vladimir Tsurkan, Norbert Büttgen, István Kézsmárki

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# Probing multiferroic order parameters and domain population via nuclear spins

M. Prinz-Zwick<sup>1</sup>, T. Gimpel<sup>1</sup>, K. Geirhos<sup>1</sup>, S. Ghara<sup>1</sup>, C. Steinbrecht<sup>1</sup>, V. Tsurkan<sup>1,2</sup>, N. Büttgen<sup>1</sup>, and I. Kézsmárki<sup>1</sup>

<sup>1</sup>*Experimental Physics V, Center for Electronic Correlations and Magnetism, University of Augsburg, 86159 Augsburg, Germany*

<sup>2</sup>*Institute of Applied Physics, Chisinau, Republic of Moldova*



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Quantifying domain population in multiferroics is required to understand domain nucleation/switching processes and achieve on-demand domain control. We report an approach based on nuclear magnetic resonance spectroscopy for the accurate measurement of volume fractions of multiferroic domains in bulk crystals. We demonstrate on a benchmarking system,  $\text{GaV}_4\text{Se}_8$ , that the electric quadrupole interaction of the  $^{71}\text{Ga}$  and the hyperfine field at the  $^{51}\text{V}$  nuclei are proper microscopic probes of the ferroelectric polarization and the ferromagnetic moment, respectively. We use the anisotropy of these local quantities to determine the multiferroic domain population, controlled here by both electric and magnetic fields. The sensitivity of this local-probe technique to site symmetries facilitates domain quantification in a wide range of anisotropic magnets, ferroelectrics, and multiferroics.

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## I. INTRODUCTION

Domains in ferroic materials, that are regions with different orientations of the order parameter, have been found to form versatile architectures with unique functionalities of the domain walls (DWs) separating them [1–10]. Domains emerging in multiferroic materials where magnetic order is accompanied by ferroelectricity or ferroelasticity represent a novel class of domains that is of fundamental interest as cross-coupling phenomena, such as the magnetoelectric effect, can lead to additional functionalities beyond the realm of (mono)ferroic DWs and open up new ways of domain control [11–14].

In type-I multiferroics, where magnetic orders develop within a structurally distorted state, different ferroelectric and/or ferroelastic domain states are also distinguished via their specific microscopic magnetic interactions. Most evidently, the principle axes of magnetic anisotropy, usually linked to the main crystallographic axes, vary between the different structural domain states. This facilitates the control of such domains via magnetic fields [9,10,15] in addition to their more common electric [16] and strain control [17]. Moreover, at atomically sharp structural DWs where the magnetic interactions show a steplike change, new magnetic states can emerge, which are nonexistent in the bulk [9]. In type-II multiferroics where magnetic and ferrodistorive orders emerge hand in hand, the coupling of different degrees of freedom can also lead to complex magnetic states with strong magnetoelectric and/or magnetoelastic effects [13]. This can provide new paths for domain control, such as the interconversion between domains and DWs [18].

Recently, complex domain structures, such as the six-fold vortex domains in ferroelectric hexagonal manganites [19–21] and the magnetic skyrmions in noncentrosymmetric magnets [22–26], have been attracting a great interest

due to their topologically protected structure. In this context, magnetic skyrmions are essentially nanometric cylindrical domains, forming periodic lattices when the DW energy becomes negative due to the Dzyaloshinskii-Moriya interaction [27]. Whether these topologically protected polar or magnetic states can lead to technological breakthroughs in electronics or spintronics depends on our understanding about domain nucleation and stability in such materials. First of all, this requires methods for quantifying domain populations.

Although there have been great advances made in the imaging of structural, ferroelectric, and magnetic domains by techniques that are surface sensitive or limited to small sample thicknesses [28–30], such as scanning probe microscopy methods, second-harmonic generation, high-resolution transmission electron microscopy, magnetic circular dichroism microscopy, methods that are capable of the precise quantification of domain populations in bulk materials are less developed. This is particularly the case for magnetic and multiferroic domains in bulk samples where polarized neutron diffraction is often the only approach to study the domain population [31]. Conventional magnetization and polarization measurements cannot be used to quantify domain populations unless there are only two ( $\pm$ ) domain states coexisting. This motivates our paper together with former nuclear magnetic resonance (NMR) spectroscopy studies on multiferroics with spiral spin structure [32–35] to demonstrate that multinuclei NMR spectroscopy can probe different order parameter simultaneously and, hence, can provide quantitative information about the volume fractions of different domain states either purely structural or magnetic or both by probing domain-specific microscopic quantities.

In the present paper, we use  $\text{GaV}_4\text{Se}_8$  as a benchmark system to demonstrate the power of NMR spectroscopy in the quantification of multiferroic domains. This compound belongs to a novel class of multiferroic materials, the lacunar

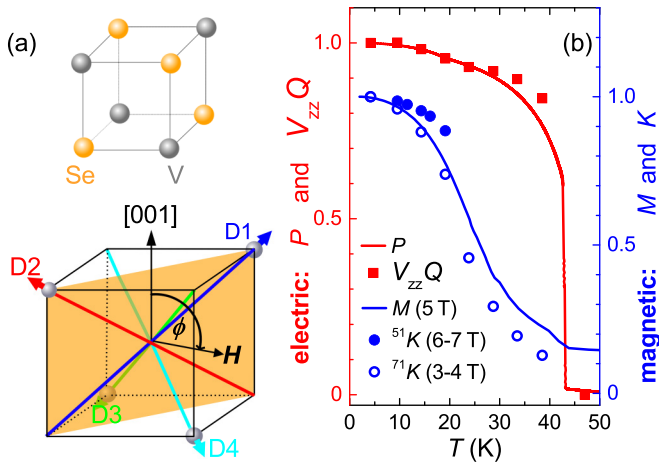


FIG. 1. (a) V<sub>4</sub>Se<sub>4</sub> cluster (top) and the four polar/anisotropy axes (bottom) in GaV<sub>4</sub>Se<sub>8</sub>. The color code of these axes,  $\mathbf{P}_1 = [111]$ ,  $\mathbf{P}_2 = [\bar{1}\bar{1}1]$ ,  $\mathbf{P}_3 = [\bar{1}1\bar{1}]$ , and  $\mathbf{P}_4 = [1\bar{1}\bar{1}]$ , indicates the contributions of the corresponding domain states, D1–D4, in all other figures.  $\mathbf{H}$  is rotated within the (1 $\bar{1}$ 0) plane (orange), where  $\phi$  is the angle between the  $\mathbf{H}$  and the [001] axes. (b) Temperature dependence of the quadrupole coupling  $eV_{zz}Q/h$  for <sup>71</sup>Ga (red symbols), the macroscopic ferroelectric polarization  $P$  (red line), the NMR line-shift  $K$  for <sup>51</sup>V / <sup>71</sup>Ga (full/open blue symbols), and the bulk magnetization  $M$  (blue line). (Signal from <sup>51</sup>V could be traced only < 20 K due to fast  $T_2$  relaxation). All quantities are normalized by their values at 4 K (<sup>51</sup>K = −33.6%, <sup>71</sup>K = 8.8%).

spinel, which have recently attracted attention as the first bulk hosts of Néel-type skyrmions [36–38] that are also dressed with ferroelectric polarization [9,10,39–41].

Lacunar spinels with the chemical formula of  $AB_4X_8$ , crystallize in a cubic structure where two types of clusters  $AX_4$  and  $B_4X_4$  form a NaCl-like lattice. In GaV<sub>4</sub>Se<sub>8</sub>, GaV<sub>4</sub>Se<sub>8</sub>, and GaMo<sub>4</sub>Se<sub>8</sub>, the degeneracy of the  $B_4X_4$  cluster orbitals drives a cooperative Jahn-Teller distortion [40,42–44], which reduces the symmetry from cubic  $F\bar{4}3m$  to rhombohedral polar  $R3m$ .

In GaV<sub>4</sub>Se<sub>8</sub>, the polar distortion at  $T_{JT} = 42$  K leads to an elongation of the V<sub>4</sub> tetrahedra along one of the four body diagonals of the cubic structure [41]. Due to the lack of inversion symmetry in the parent  $F\bar{4}3m$  structure, there are no domains with reversed polarization coexisting ( $\pm P$  domains), instead, there are only four domain states with the corresponding polarizations spanning 109° as shown in Fig. 1(a). The polar axis of a given domain is, at the same time, the axis of uniaxial anisotropy [37,45]. Correspondingly, below  $T_{JT}$ , there are four domain states each having a distinct magnetic easy axis. Below the magnetic ordering temperature  $T_C = 18$  K, GaV<sub>4</sub>Se<sub>8</sub> hosts various magnetic phases, including a cycloidal and a Néel-type skyrmion lattice state [37,38,41]. Due to the uniaxial magnetic anisotropy, the magnetic phase diagram depends not only on the magnitude, but also on the orientation of the magnetic field, thus, it is specific to the different domain states [9]. Moreover, due to the axial distortion, the rhombohedral domains can be controlled both via electric and magnetic fields [9,10,15].

Here, we show that in addition to the anisotropic electron spin susceptibility, the rhombohedral distortion in GaV<sub>4</sub>Se<sub>8</sub> also leads to an anisotropy of the hyperfine coupling at the

<sup>51</sup>V nuclei which we exploit to measure the volume fractions of the different rhombohedral polar domains at  $T < T_C$  where the compound becomes multiferroic. Moreover, we show that the so-called quadrupole splitting of the <sup>71</sup>Ga NMR line as another consequence of the polar distortion offers a complementary path to determine the domain population in GaV<sub>4</sub>Se<sub>8</sub>.

## II. EXPERIMENTAL TECHNIQUE UTILIZING V<sub>4</sub>Se<sub>4</sub> CLUSTER NMR

We recorded field-swept NMR spectra at  $\nu = 51$  MHz using a phase-coherent homebuilt spectrometer in a homodyne mode. At first, we investigated an unpoled single crystal of GaV<sub>4</sub>Se<sub>8</sub> (with mass 9.22 mg, grown via chemical transport reaction [40], diameter  $\approx 1$  mm). As demonstrated in Fig. 1(b), NMR studies on <sup>51</sup>V (with nuclear spin  $I = 7/2$ ) and <sup>71</sup>Ga ( $I = 3/2$ ) provide access to both the electric- and the magnetic-order parameters. The ferroelectric polarization  $P$  can be detected via the quadrupole coupling  $eV_{zz}Q/h$  that is induced by the interaction of the electric quadrupole moment  $Q$  of the <sup>71</sup>Ga nucleus with the local electric-field gradient  $V_{zz}$  [46], emerging below  $T_{JT}$ . The magnetization and its orientation can be probed locally via the line-shift  $K$  of <sup>51</sup>V and <sup>71</sup>Ga nuclei, originating from the internal magnetic field of the unpaired  $d$  electron at the V<sub>4</sub> cluster, shown in Fig. 1(a). Figures S1 and S2 in the Supplemental Material [47] display the spectra from which these parameters were extracted.

In all experiments, the applied magnetic-field  $\mathbf{H}$ , irrespective of its orientation, was strong enough to set the material to the field-polarized ferromagnetic state with the electron magnetization being parallel to the field [37,41]. Thus, the dependence of the NMR spectra on the orientation of  $\mathbf{H}$ , that was rotated within the (1 $\bar{1}$ 0) crystallographic plane [see Fig. 1(a)], fully originates from the anisotropy of the hyperfine coupling, induced by the polar rhombohedral distortion. The population of the multiferroic domains was controlled by poling the crystals through  $T_{JT}$  using static electric or magnetic fields. Due to fast  $T_2$  relaxation of the <sup>51</sup>V nuclei, a rather short pulse sequence was chosen, using 4- $\mu$ s solid-echo pulses separated by a 25- $\mu$ s pulse separation time.

The rhombohedral transition is expected to split the <sup>51</sup>V line into four peaks for arbitrary directions of  $\mathbf{H}$ , where each peak is associated with one type of domain. In fact, Figs. 2(a) and 2(b) reveal an unusually strong anisotropy of the hyperfine field at 4.2 K. Four <sup>51</sup>V lines, one for each domain state, are resolved and the resonance fields vary within  $4.6 < \mu_0 H_{\text{Res}} < 7.3$  T.

Upon the rotation of  $\mathbf{H}$  within the (1 $\bar{1}$ 0) plane as sketched in Fig. 1(a), the field passes through the anisotropy (polar) axes of the D1 and D2 domains. For these two domains, the resonance field curve in Fig. 2(a) passes through a minimum/maximum when  $\mathbf{H}$  is parallel/perpendicular to the anisotropy axis. For the other two domain states, the angle spanned by  $\mathbf{H}$  and their anisotropy axes varies between 54° and 90° upon the rotation of  $\mathbf{H}$ , thus, only the maximum of  $H_{\text{Res}}$  is observed. Ideally, the resonance-field curves of these D3 and D4 domains should fully overlap, and all four curves should cross each other when  $\mathbf{H}$  points along the [001] axis. Deviations from this behavior are caused by a small misalignment of  $\sim 4^\circ$ , which allows us to resolve four distinct lines at

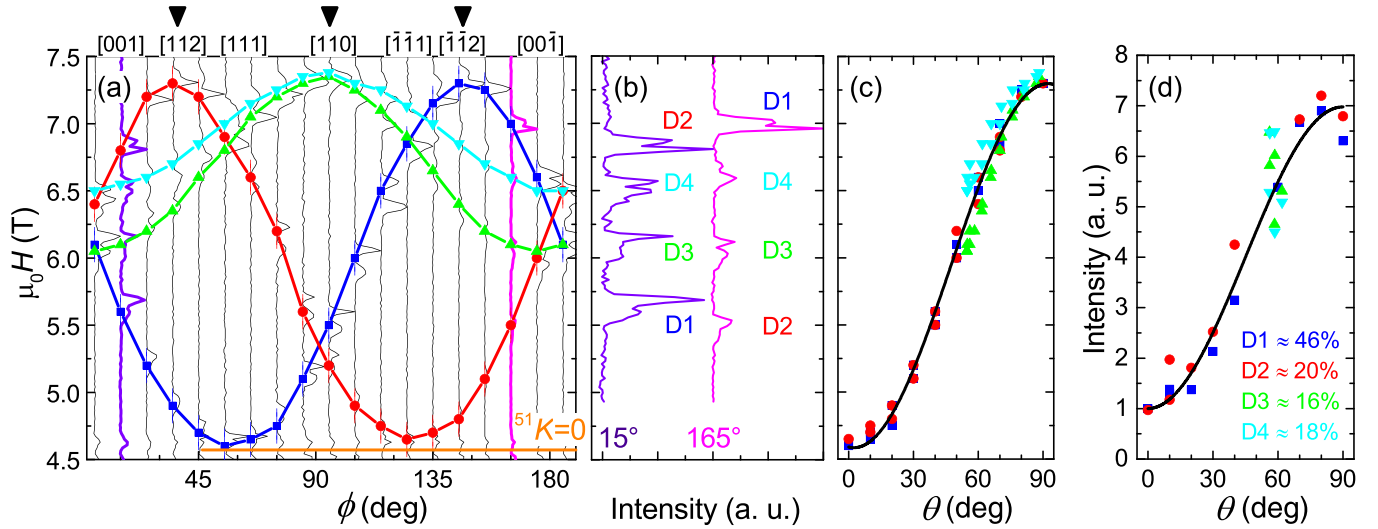


FIG. 2. (a) Dependence of the  $^{51}\text{V}$  NMR spectra on the orientation of  $\mathbf{H}$ , at 51 MHz at 4.2 K. Individual field-swept spectra (gray lines) are displayed at the respective angles. Spectra at  $\phi = 15^\circ$  and  $165^\circ$ , respectively, highlighted by purple and pink colors, are enlarged in panel (b). The angular dependence of the  $^{51}\text{V}$  resonance fields corresponding to domains D–D4, are traced by lines with colors chosen according to Fig. 1(a). The diamagnetic reference field  $^{51}\text{K} = 0$  of the  $^{51}\text{V}$  nuclei is shown by the horizontal orange line. (c)/(d) Resonance field  $H_{\text{res}}$ /intensity  $I$  versus  $\theta$ , the angle spanned by  $\mathbf{H}$  and the polar axes of the respective domains. In panel (d), the intensity values for the different domains are scaled according to the percentages indicated in the figure, which correspond to the volume fraction of the domains. Solid black lines indicate the  $\sin^2 \theta$  dependence of  $H_{\text{res}}$ . Panels (a)–(c) share a common vertical scale. All data were collected on an unpoled crystal.

arbitrary orientations of  $\mathbf{H}$  as exemplified by two spectra in Fig. 2(b).

Intensities of the four lines contain information about the volume fractions of the four domains. However, the volume fraction is not the only factor determining the relative intensities since they also vary with the orientation of  $\mathbf{H}$  as obvious from Fig. 2(b), which can also be followed in Fig. 2(d). To reveal the angular dependence of the line intensities, in Figs. 2(c) and 2(d), we plot the fields  $H_{\text{res}}$  and the intensities of the four lines versus the angle  $\theta$ , spanned by  $\mathbf{H}$  with the anisotropy axes of the corresponding domains. The resonance field follows an angular dependence common for all domains, according to  $H_{\text{res}}(\theta) = H_0 + A \sin^2 \theta$ , where  $\mu_0 H_0 = 4.55$  T is the resonance field of the diamagnetic  $^{51}\text{V}$  nucleus at 51 MHz and  $A$  is the anisotropy of the hyperfine field. Since  $H_{\text{res}}$  is always higher than or equal to  $H_0$ , the local internal field at the  $^{51}\text{V}$  nuclei points opposite to the applied field. The internal field at the  $^{51}\text{V}$  nuclei likely originates from the magnetic moment of the unpaired electron on the same  $\text{V}_4$  cluster via contact and dipolar terms, whereas intercluster hyperfine interactions likely give a minor contribution, similar to  $\text{GaV}_4\text{S}_8$  [48,49].

The intensities of all domains follow the same angular dependence of  $H_{\text{res}}$ , i.e., they also exhibit a simple  $\propto \sin^2 \theta$  dependence as demonstrated in Fig. 2(d). Therefore, the intensity curves all collapse on each other after normalization. Importantly, the angular-independent normalization factors lead to the volume fractions, listed as a legend in Fig. 2(d).

As additionally seen in Fig. 2(b), all four  $^{51}\text{V}$  lines exhibit weak splittings due to quadrupolar interactions and the inequivalence of vanadium sites within the distorted  $\text{V}_4$  clusters. Since these splittings, partly resolved in the field-swept spectra, are not relevant in the process of domain quantifica-

tion, the overall intensities of the four lines were obtained by integration over these fine structures.

### III. DOMAIN QUANTIFICATION UNDER ELECTRIC AND MAGNETIC DOMAIN CONTROLS

Next, we describe a more precise approach for domain quantification where the angular dependence of the intensity does not play a role and the line intensities directly measure the volume fractions of the corresponding domain states, reducing possible errors caused by misalignments or low signal/noise ratios for small polar angles in the previous semi-quantitative approach. In the second scheme, the NMR spectra are measured in such configurations that the same orientation of  $\mathbf{H}$  with respect to the anisotropy axis is realized for each domain state in one of the configurations. As seen in Fig. 2(a) when the field is rotated within the  $(1\bar{1}0)$  plane, there are three configurations where  $\mathbf{H}$  is perpendicular to some of the four anisotropy axes, thus, the resonance fields of the corresponding domains are the same. This holds for the D2 and the D1 domains at  $\phi = 35^\circ$  and  $145^\circ$ , respectively, and for both the D3 and the D4 domains at  $90^\circ$ . Under this condition, the relative intensities depend solely on the domain population, whereas angular-dependent effects, coming, e.g., from  $T_2$  relaxation, cancel out. Hence, by comparing the intensities of the lines at these three angles, where they are located at the maximum  $\mu_0 H_{\text{res}} \approx 7.3$  T, one can uniquely determine the volume fractions of the D1 and the D2 domains and the sum of the D3 and the D4 domains as presented in the middle column of Fig. 3(a). Note that the percentages roughly agree with those given in Fig. 2(d), whereas the previous approach has larger uncertainties. Next, this method is used to trace changes in domain population upon electric or magnetic control.

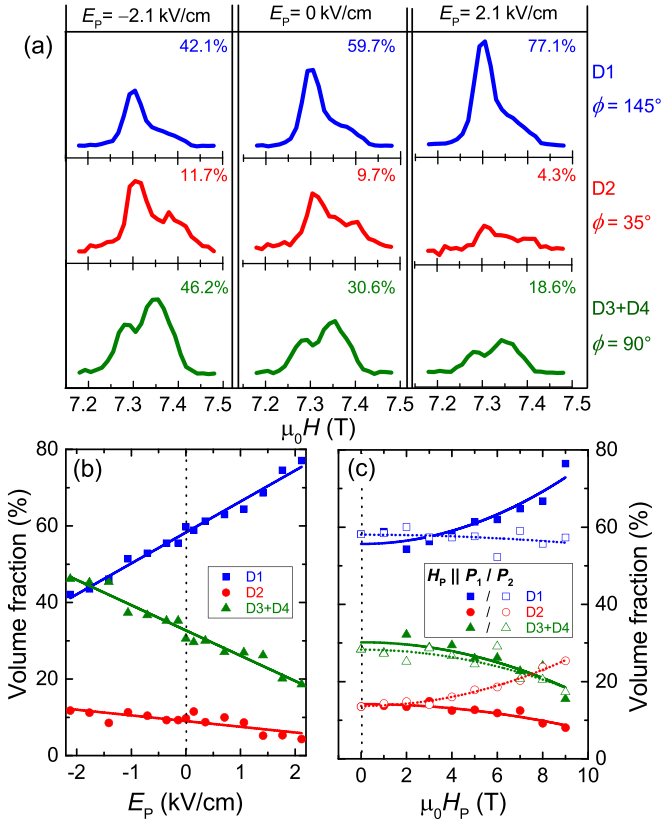


FIG. 3. (a)  $^{51}\text{V}$  spectra of different domains measured after electric poling with three different strengths of  $\mathbf{E}_p \parallel \mathbf{P}_1$ . Data for each poling are in separate columns. The spectra of different domains, in separate rows, were measured at such orientations of  $\mathbf{H}$  where the resonance field is the maximal  $H_{\text{res}} = 7.3$  T for the corresponding domain [D1:  $\phi = 145^\circ$ , D2:  $\phi = 35^\circ$ , D3 + D4:  $\phi = 90^\circ$ , see black top arrows in Fig. 2(a)]. Although spectra in each row are plotted on a common intensity scale to track poling induced changes in the population of the corresponding domains, the intensity scales of the different rows are chosen arbitrarily to optimize visibility. The relative intensities of all lines, i.e., the volume fractions of the respective domains, are given in percentages. (b) and (c) Volume fractions of the different domain states as a function of the poling electric/magnetic-field  $E_p/H_p$ . In the latter, results of poling with both  $\mathbf{H}_p \parallel \mathbf{P}_1$  and  $\mathbf{H}_p \parallel \mathbf{P}_2$  are shown. The linear/quadratic fits correspond to the linear/quadratic  $E/H$  dependence of the free energy, which is reflected in the poling efficiency [15].

The domain population was controlled by cooling the sample through  $T_{\text{IT}}$ , whereas applying poling electric or magnetic fields along the [111] axis, the anisotropy/polar axes of the D1 domain. Correspondingly, one expects the promotion and the suppression of this domain state by positive and negative electric fields, respectively [15]. Figure 3(a) shows that the D1 domain is naturally favored, i.e., it has the largest population even without electric poling, and its population follows the tendency expected for positive and negative poling electric fields. The effect of electric poling on all domain states can be observed in more details in Fig. 3(b). In contrast, the effect of magnetic poling should not depend on the sign of the poling field as the magnetic anisotropy energy is an even function of  $\mathbf{H}$  [15]. Indeed, we observe in Fig. 3(c) that the populations of

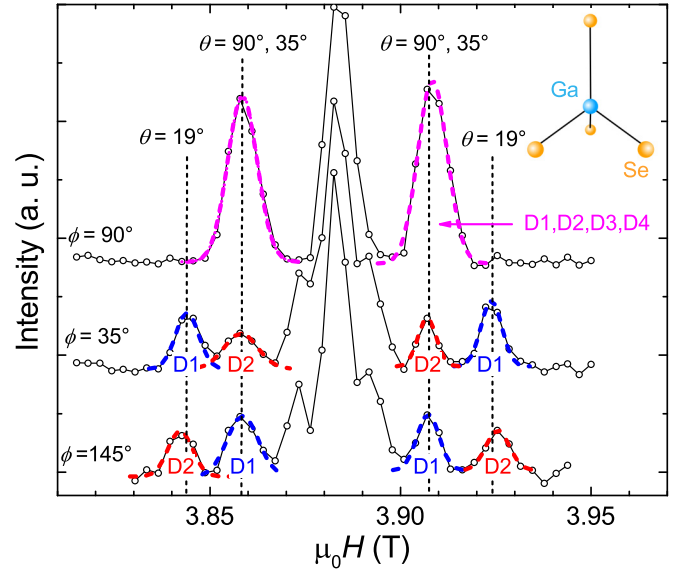


FIG. 4.  $^{71}\text{Ga}$  spectra at 38.5 K and 51 MHz for three orientations of the magnetic-field  $\phi = 35^\circ$ ,  $90^\circ$  and  $145^\circ$ . In addition to the central line at  $\sim 3.88$  T, quadrupolar satellites are resolved. Values of  $\theta$ , i.e., the angle between  $\mathbf{H}$  and the polar axes of the domains, are indicated for each satellite pair together with the domains contributing to the satellites.

the different domains change quadratically with the magnetic field.

Our microscopic domain quantification method was validated via the simultaneous investigation of the domain population using macroscopic pyroelectric current measurement (for more details, see Fig. S3 of the supplemental Material [47]). However, this macroscopic control method has strong limitations as it cannot quantify the fraction of the different domain states (D1  $\dots$  D4) separately. Instead, it measures the overall polarization  $P$ , that is related to the individual volume fractions  $V$  according to  $P = P_0[V_{D1} - (V_{D2} + V_{D3} + V_{D4}) \cos 71^\circ]$ , where  $P_0$  is the magnitude of the saturation polarization.

We carried out another independent validation of the domain quantification technique using the other nuclear probe, namely, the quadrupole splitting of  $^{71}\text{Ga}$ . In the finite magnetic field, the  $^{71}\text{Ga}$  line splits into three lines: A central line and two symmetric satellites. In the field-swept spectrum, the distance between the two satellite lines is given by [46]

$$\Delta H = \frac{3\pi eV_{zz}Q}{\gamma h I(2I - 1)}(3 \cos^2 \theta - 1). \quad (1)$$

Note that  $\Delta H$  carries domain-specific information as an arbitrarily orientated field spans different angles with the polar axes of the domains. In strong contrast to the low-temperature behavior of the  $^{51}\text{V}$  spectrum, the  $^{71}\text{Ga}$  spectrum at temperatures  $T_C < T < T_{\text{IT}}$  is governed by the quadrupole splitting as the anisotropy of the hyperfine coupling is negligible, thus, the angular dependence of the spectra are well described by Eq. (1).

The domain quantification is demonstrated in Fig. 4, where three  $^{71}\text{Ga}$  spectra of an unpoled crystal are shown for  $\phi = 90^\circ$ ,  $35^\circ$ , and  $145^\circ$ , the angles highlighted by black arrows



in Fig. 2(a). For the first angle, we only expect and observe two satellites since  $\Delta H$  has the same value for all four domains. In the  $\phi = 35^\circ$  and  $145^\circ$  spectra, the satellites of the D1 and D2 domains can be resolved separately, whereas the satellites of D3 and D4 domains strongly overlap with the central peak. From these three spectra the volume fractions of the domains can be determined,  $D1 \approx 28\%$ ,  $D2 \approx 20\%$ , and  $D3 + D4 \approx 52\%$ . These values closely reproduce those obtained within the same cooling run using the former procedure based on the anisotropic hyperfine coupling of  $^{51}\text{V}$ , namely,  $D1 \approx 27\%$ ,  $D2 \approx 21\%$ , and  $D3 + D4 \approx 52\%$ .

#### IV. CONCLUSION

In conclusion, we developed a method for the quantification of domain populations in bulk magnetic, ferroelectric, and/or ferroelastic as well as multiferroic crystals. Domains are selectively probed via the distinct response of the nuclear spins in the different domains. In externally applied magnetic fields, the NMR spectrum becomes domain specific since it depends on the relative orientation of the order parameters and the external field, which has been exploited to determine

the fraction of spin spirals with different ordering vectors [32–35]. In  $\text{GaV}_4\text{Se}_8$ , we demonstrate that magnetic domains are easily distinguishable via the anisotropy of the hyperfine coupling since the orientation of the anisotropy axes are dictated by domain-specific lattice distortions. Similarly, domains are also efficiently distinguished by the orientation of the local electric-field gradient at polar sites, probed via nuclear quadrupole interaction. The former approach is applicable to any nucleus, whereas the second one requires nuclei with finite quadrupole moments. The possibility to probe the magnetic and electric order parameters simultaneously can give a microscopic insight into the origin of multiferroicity in new systems. Concerning symmetry requirements, these methods can work whenever the crystal symmetry is lower than cubic, which is the case for ferroic domains, in general. Thus, our method is applicable for a wide range of materials.

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