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Chromium doped NH$_2$(CH$_3$)$_2$Ga(SO$_4$)$_2$ × 6H$_2$O crystal – representative of a new family of magnetoelectric materials

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Abstract

The paper is devoted to the detailed study of electric and magnetic properties and magnetoelectric interactions in NH$_2$(CH$_3$)$_2$Ga(SO$_4$)$_2$ × 6H$_2$O crystals doped with chromium—DMAGaS:Cr. The temperature dependence of the specific heat revealed clear evidence of a series of phase transitions related to the electric dipoles ordering. The different types of the DMA cation ordering in the structure of DMAGaS:Cr were evidenced in the temperature evolution of the EPR spectra. In addition, a considerable magnetoelectric coupling was demonstrated within the paramagnetic and ferroelectric phase of DMAGaS:Cr crystal. In the narrow temperature range in the vicinity of the Curie point, this crystal was found to possess the largest values of the coefficient of ME interaction as well as the largest magnetodielectric effect within the family of ferroics with organic cation. The model describing the ME effect was proposed. The magnetic field through the magnetostriction effect changes the level of the local lattice deformations caused by metal ion substitution. The applied magnetic field changes Cr-Cr distances and modifies the hydrogen bonds and process of DMA group ordering, affecting spontaneous polarization.

1. Introduction

The magnetoelectric (ME) effect in ferroics has been intensively studied in the last decades, challenging modern physics of solid state [1,2] and spintronics [3–6]. In particular, a realization of the electric control over magnetization in the ferroics looks very attractive for creation of the magnetic memory devices with a low dissipation of power. Although the coexistence of spontaneous polarization and magnetization is an important factor in the search for new magnetoelectric materials [7–9], these two phenomena usually are hardly observable in a single phase [10,11]. Moreover, the magnetic ordering and, respectively, the magnetoelectric effect mostly occur in the ferroics at temperatures very close to 0 K. Under such circumstances, the scientists would concentrate their efforts on the investigations of the higher order ME effects that are not dependent on symmetry conditions [12,13]. On the other hand, the organic-inorganic ferroics have to be considered as an alternative. For example, a ME coupling was found in the paramagnetic [(CH$_3$)$_2$NH$_3$][Mn(HCOO)$_6$] [14]. Together with other related compounds [15–21], this family of materials looks very beneficial for the search of ME coupling [22,23].

Taking into account that the ferroelectric ordering is realized in the numerous organic-inorganic ferroics [24–38], the substitution of the metal ion in the inorganic anionic complexes would give the possibility to introduce the magnetic ordering into a previously diamagnetic matrix. In such a way using, for example, the partial metal ion substitution one can generate the magnetoelectric effect in the known ferroelectric material. Indeed, as it was shown in our recent study [38], NH$_2$(CH$_3$)$_2$Al(SO$_4$)$_2$ × 6H$_2$O (furthermore—DMAAlS) crystals were transformed from the diamagnetic to the paramagnetic state [33,34] within their ferroelectric...
phase. These crystals undergo a second-order transition into the ferroelectric phase at $T_c = 152$ K at cooling. The isomorphous substitution of metal ions in the above-mentioned compound provided the possibility of its magnetic and ME properties engineering [36, 37]. Indeed, the paramagnetic state [38] and large ME effect were generated in DMAAlS due to the partial substitution of aluminum with chromium [38]. Moreover, it was shown that the sign of the ME coefficient may be tuned by the change of Cr$^{3+}$ content. The corresponding phenomenological description of the observed magnetoelectric coupling in this solid solution was presented in the paper [39].

Synthesis of new multiferroic materials by modification of the well-known ferroelectrics shown in the example of DMAAlS crystal doped with chromium provides the possibility of step-by-step tuning of their electric and magnetic properties. In principle, such an approach allows to synthesize the magnetic multiferroics with the largest values of the ME coupling coefficient within the appropriate temperature range. In this respect, chromium doped NH$_2$(CH$_3$)$_2$Ga(SO$_4$)$_2$ \times 6H$_2$O ferroelectric crystals, that are close to DMAAlS by their chemical formula and properties, look very attractive as the objects for the study of possible magnetic ordering and magnetoelectric effect. Their investigations open a new degree of freedom connected with the substitution of the non-magnetic metal ion of the matrix in addition to its substitution with the magnetic Cr$^{3+}$ ion.

The initial NH$_2$(CH$_3$)$_2$Ga(SO$_4$)$_2$ \times 6H$_2$O crystals (abbreviated as DMAGaS) were already widely studied. Their structure [40] consists of Ga(H$_2$O)$_6$ octahedra, SO$_4$ tetrahedra and dimethylammonium (NH$_2$(CH$_3$)$_2$)$^+$ or DMA) cations. These complex ions are united into a three-dimensional framework of hydrogen bonds. At cooling DMAGaS undergoes a first-order phase transition (PT) at $T_{c1} = 134$ K into the ferroelectric phase with the change of symmetry $2/m \rightarrow m$. Ordering of the dimethylammonium cations carrying a dipole moment was found to be responsible for this phase transition [40]. The ferroelectric phase is limited by the I order phase transition at $T_{c2} = 106$ K (at cooling) which is characterized by a considerable thermal hysteresis (up to 12 K) [41]. According to other data, the ferroelectric phase in DMAGaS lies between the temperatures $T_{c1} = 136$ K and $T_{c2} = 119$ K (at heating) [42].

The influence of the partial substitution of metal ions on the dielectric dispersion in NH$_2$(CH$_3$)$_2$Ga$_{1-x}$Cr$_x$(SO$_4$)$_2$ \times 6H$_2$O (x = 0; 0.065) crystals was investigated by the authors of the paper [43]. It has been found that the substitution of Ga with Cr is followed by considerable changes in the parameters describing the dielectric relaxation process, first of all, by an increase of the relaxation time $\tau$. Such a phenomenon was explained in the following way. Cr ions, due to their smaller size in comparison with Ga ions, cause the appearance of the local lattice distortions promoting the formation of the larger dipole clusters around the Curie point $T_{c1}$ [43]. One can suppose that partial substitution of Ga with Cr also will be followed by the increased magnetic correlations and possible magnetoelectric coupling in Cr-doped DMAGaS, similarly to the case of DMAAlS analogue with aluminum ions partially substituted with chromium ions. Under such circumstances, this paper was devoted to the detailed study of the electric and magnetic properties and magnetoelectric coupling in DMAGaS crystals doped with chromium—DMAGaS:Cr. It is important to note that this crystal undergoes a first-order ferroelectric phase transition contrary to the case of the crystals with aluminum which implies considerable changes in the ME coupling.

2. Method

Single DMAGaS:Cr crystals were grown by a slow evaporation method from the water solution of gallium and chromium sulfates, taken in the molar ratio 1:0.007, and dimethylammonium sulfate at a constant temperature.

The dielectric permittivity was investigated on the basis of the capacitor capacitance measurements on the samples cut normally to the ferroelectric $a$ axis. The polished samples were covered with conducting silver paste electrodes. The measurement of spontaneous polarization and dielectric parameters in an external magnetic field was performed using a Quantum Design PPMS system. The Andeen-Hagerling 2700A bridge was used for measurements of the capacitance. The ferroelectric hysteresis loops were measured in an external electric field with a frequency of 0.01 Hz using the Keithley 6517B electrometer. The temperature changes of spontaneous polarization were determined on the basis of temperature dependences of pyrocurrent, measured by Keithley 6517B electrometer. The maximum value of the magnetic field while measuring the electrical properties was equal to 9 T. The magnetic moment measurement within the range of 1.8–300 K and magnetic fields up to 7 T was performed using the Quantum Design MPMS3 system. The crystal was attached to the quartz holder to avoid the background signal, and the core diamagnetic contribution of the sample was subtracted using Pascal’s constants. The magnetic field was applied within the bc-plane. The EPR experiments were performed using an ESR910 helium flow-type cryostat combined with a Bruker ELEXSYS II E500 X-band spectrometer in the temperature range of 5–290 K. The heat capacity was measured with the employment of a Quantum Design PPMS system in the temperature range between 2 K and 300 K in a zero magnetic field using the same crystal as used in magnetic measurements.
3. Results

The temperature dependence of magnetic susceptibility of DMAGaS:Cr crystals measured in the applied magnetic field of 0.1 T shows a paramagnetic behavior originating from the presence of Cr$^{3+}$ ions in a diamagnetic matrix of DMAGaS. The Cr$^{3+}$ substitutes the Ga$^{3+}$ ions in the center of octahedral voids formed by water molecules in the studied structures. In the temperature dependence of the effective magnetic moment $\mu_{\text{eff}}/\mu_B$ depicted in figure 1, small deviations from a constant value of $\mu_{\text{eff}}/\mu_B$ appear below 180 K. Interestingly, no anomaly is seen at the ferroelectric phase transition point $T_{c1}$ as it would be expected from previous studies [44–47]. The Cr$^{3+}$ ions in octahedral coordination are in $3d^6$ electronic configuration with $S = 3/2$ spin state, and the concentration of the substituted Ga$^{3+}$ sites can be estimated from $\mu_{\text{eff}}/\mu_B$ or saturation magnetization at low temperatures. The field dependence of the magnetization measured at low temperatures is shown in the inset of figure 1. The magnetization value at 1.8 K is close to the saturation at 7 T and reaches only 0.0214 $N_A\mu_B$ in comparison to the expected 2.97 $N_A\mu_B$ for a full substitution rate ($S = 3/2$ and $g = 1.98$).

The magnetization curve measured at 1.8 K was fit to the Brillouin function yielding the concentration of Cr$^{3+}$ ions to be 0.71%. The influence of the very small single-ion anisotropy of Cr$^{3+}$ ions [45] can be neglected in this analysis. Such a low substitution rate is in agreement with the room temperature value of $\mu_{\text{eff}}/\mu_B$ in comparison to 3.83 $\mu_B$ expected for complete substitution.

The Cr$^{3+}$ ion substituted in Ga$^{3+}$ site in DMAGaS represents a sensitive probe of the DMA cation ordering in the crystal structure, which is important for the electric properties of the studied samples. As the temperature dependence of the effective magnetic moment showed, subtle changes in the coordination environment of Cr$^{3+}$ ions were revealed already at 180 K.

Therefore, we have studied X-band EPR spectra of DMAGaS:Cr to evidence the gradual changes in the DMA cation order as described in references [45–47]. A powdered sample was studied from 290 K down to 5 K to capture all features. The obtained changes in the EPR spectra are in good agreement with references [45–47], four distinct temperature regions can be identified (as emphasized by the colored background of figure 2), which were previously assigned to the paraelectric and ferroelectric phases, the intermediate region with strong DMA disorder and incommensurability and, finally, the antiferroelectric phase when the temperature is decreased. The influence of the single-ion anisotropy of Cr$^{3+}$ ions can be described by a Hamiltonian

$$H = \hat{S}\hat{D}\hat{S} + \mu_B \hat{g}\hat{S}$$  \hspace{1cm} (1)

where is the electron spin operator, B is the applied magnetic field, and $\hat{D}$ represents the single-ion anisotropy tensor. The parameters D and E of single-ion anisotropy from the so-called spin Hamiltonian notation are related to through its principal values $D = (3/2)D_{xx}$ and $E = (D_{yy} - D_{zz})/2$. The same parameters of the single-ion anisotropy and g-factor as obtained from a single-crystal study [45] were used to simulate the powder EPR

![Figure 1. The effective magnetic moment of DMAGaS:Cr as a function of temperature. Inset: field dependence of the magnetization at 1.8 K (red circles) and 5 K (blue squares), including the fit of the Brillouin function for $S = 3/2$ and $g = 1.98$ (solid black line), revealing a 0.71% substitution of Ga$^{3+}$ by Cr$^{3+}$ ions.](image-url)
spectra at 290 K and 120 K, as shown in figure 2, in the paraelectric and ferroelectric phase, using EasySpin simulation package [48]. The set of the parameters used for the simulation was $g = 1.982$, $D = 0.089$ cm$^{-1}$, and $E = 0.013$ cm$^{-1}$ for 290 K and $g = 1.982$, $D = 0.1088$ cm$^{-1}$, and $E = 0.0013$ cm$^{-1}$ for 120 K. A simple isotropic convolutional line broadening of 11 mT was applied in the simulation. The overall agreement of the simulated spectra with the experimental ones confirms that for a substitution rate in our sample, the single-ion parameters are identical to the ones observed earlier in doped DMAGaS. We have also attempted to simulate the spectra below 60 K in the antiferroelectric phase, but the one set of the parameters obtained in [45, 46] does not capture all the features of the powdered spectra. Although there are four structural configurations formed by the arrangement of the two neighboring DMA cations yielding four nonequivalent magnetic sites, only different orientations of the principal axes of the $\mathbf{D}$-tensor were assumed [46]. We speculate that a slight change of the $D$ and $E$ for each nonequivalent Cr$^{3+}$ site (or statistical distribution of parameters, $D$-strain) is possible, maybe due to the substitution inhomogeneity. Interestingly, a subtle change in $\mu_{\text{eff}}$ was observed at temperatures about 180 K (see figure 1) that is connected with the slowing down of the fast reorientation of DMA cations that also yields the fine structure splitting of some EPR lines in figure 2 as suggested in references [45, 46].

The temperature dependence of specific heat is depicted in figure 3. The cascade of phase transitions is observed with decreasing temperature. The first, most significant, $\lambda$-type anomaly was observed at 135 K, followed by less pronounced anomalies at 117.6 K and 61 K (figure 3). Those anomalies separate individual phases as described above [46, 47]. The detection of mentioned distinguished temperatures in the temperature dependence of heat capacity is in excellent agreement with EPR measurement. However, EPR spectra and magnetic measurements reflect a gradual change in magnetic parameters due to the ordering of DMA molecules.

In order to detect possible magnetoelectric coupling, we investigated the dielectric permittivity as a function of temperature at different values of the applied magnetic field (figure 4). The magnetic field causes a small but noticeable change of the Curie point $T_{c1}$, which reflects itself in the temperature shift of the dielectric permittivity peak. The effect was found to be reversible and is followed by a considerable change of dielectric permittivity in the vicinity of $T_{c1}$ (figure 5). Therefore, one can conclude that DMAGaS:Cr crystal reveals the magnetodielectric effect (MDE). One can note that the change of $\epsilon'$ value practically linearly depends on the magnetic field. For the qualitative estimation of the effect, one can use the equation [49]:

$$\frac{\Delta \epsilon'(H)}{\epsilon'(0)} = \frac{\epsilon'(H) - \epsilon'(0)}{\epsilon'(0)}$$  \hspace{1cm} (2)

where $\epsilon'(H)$ and $\epsilon'(0)$ are the dielectric permittivity values with and without the applied magnetic field, respectively. The relative change of the dielectric permittivity within the range of 0–9 T was found to be 96.8 % for the temperature $134.3$ K, and 5.1 % for $T = 133.9$ K. The first of these values appeared to be even higher than in TEACCB–3 crystals manifesting the largest MDE [49]. On the other hand, in spite of the case of TEACCB–3
revealing a large effect with the relative change of the dielectric permittivity in the range from 10 up to 78 % in a wide temperature range (230–295 K), DMAGaS:Cr solid solution is characterized by a maximal effect only around the Curie point.

The magnetic field dependence of the electric polarization measured after ferroelectric saturation (figure 6) also confirms a considerable magnetoelectric coupling. The dielectric hysteresis loop was found to be saturated and symmetric with respect to the electric field direction reversal both under the applied magnetic field as well as in the case of its absence. The magnetic field dependence of the electric polarization appeared to be considerably nonlinear (figure 6, insert)—in the beginning, its value grows like in DMAAl0.8Cr0.2S and at higher fields decreases similarly to the case of DMAAl0.935Cr0.065S analogue [39]. It is necessary to note that the direction and even value of the Curie point shift caused by the magnetic field are practically the same as in DMAAl0.8Cr0.2S [39].

Additional fruitful information about the nature of the ME coupling can be obtained from the behaviour of the pyroelectric current around the ferroelectric phase transition under the external magnetic field [50, 51]. The temperature dependences of the spontaneous polarization obtained from the temperature dependences of pyrocurrent at different values of applied magnetic field confirm its considerable influence on the spontaneous polarization and the phase transition temperature (figure 7). The latter is easily obtained from the position of a jump of the spontaneous polarization.

Figure 3. The temperature dependence of specific heat of DMAGaS:Cr single crystal measured in a zero magnetic field. The colored background represents four distinct phases related to different types of electric dipole ordering (DMA cation ordering).

Figure 4. The dielectric permittivity of DMAGaS:Cr crystals as a function of temperature measured in the vicinity of the ferroelectric phase transition. In the insert—the dependence of ε’ peak position on the magnetic field.
It is necessary to note that the magnetic field shifts the phase transition point toward lower values and leads to smearing of the ferroelectric PT since the spontaneous polarization arises at higher temperatures than $T_{c1}$ in comparison with the case observed without the applied field. This effect is observed most clearly for the intermediate values of the magnetic field ($3\,T$). It is important to note that the observed effect is reversible—when the magnetic field is switched off, the value of spontaneous polarization practically returns to its initial value.

The magnetoelectric coupling coefficient describes the change in the electric polarization due to the application of the magnetic field. Taking into account that the electric polarization would be determined on the basis of the temperature dependences of the pyrocurrent density one can obtain the temperature dependences of the ME coupling coefficient $\alpha_{ME}$ (figure 8) using the equation:

$$\alpha_{ME} = \frac{1}{\Delta H} \int (I_{H=0} - I_H) dt,$$

where $H$ is the applied magnetic field and $I$ is the pyrocurrent density at the constant external magnetic field.

Analysing the temperature dependences of $\alpha_{ME}$ coefficient, one can make the following conclusions:
1. The considerable negative ME effect is observed within the ferroelectric phase of DMAGaS:Cr crystal—polarization decreases under the action of the magnetic field. The behaviour of $\alpha_{\text{ME}}$ looks very similar to those in DMAAl$_{0.935}$Cr$_{0.065}$S\cite{38, 39}, although its average value was found to be six times lower.

2. In spite of the case of DMAAl$_{1-x}$Cr$_x$S\cite{38, 39} solid solutions, the investigated crystal reveals the sharp $\lambda$-like peaks of $\alpha_{\text{ME}}$ coefficient at the Curie point, and due to this, its value exceeds those for DMAAl$_{1-x}$Cr$_x$S in the narrow range in the vicinity of $T_{c1}$. In this case, the positive ME effect takes place.

3. $\alpha_{\text{ME}}$ coefficient possesses a nonzero value in the narrow temperature range laying above $T_{c1}$, especially at the intermediate values of magnetic fields (3 T).

4. $\alpha_{\text{ME}}$ coefficient reveals a nonlinear dependence on the value of a magnetic field within the ferroelectric phase—it increases in the beginning and afterward starts to decrease at higher values of magnetic field reaching practically zero value at $H = 9$ T.

5. To provide adequate comparison of the ME coupling in different crystals of DMAMe$_{1-x}$Cr$_x$S family, it is necessary to take into account that the $\alpha_{\text{ME}}$ values in the crystals with Me = Al were determined under the influence of the magnetic field 6 T. It is clear that observed differences of ME coupling from the case of
DMAAl$_{1-x}$Cr$_x$S crystals are explained by the fact that the latter is characterised by a second-order phase transition, whereas DMAGaS:Cr undergoes the first-order PT. In particular, the second and third conclusions from those mentioned above are explained by the shift of the first-order PT under the action of the applied magnetic field and the coexistence of two phases in the vicinity of $T_{C2}$, respectively.

Observation of the ME effect in the paramagnetic phase demands a more detailed consideration. The magnetoelectric coupling arises due to the twofold effect. First of all, the embedding of magnetic Cr ion into the initially diamagnetic lattice of DMAGaS crystal generates strains and, on the other hand, causes the sensitivity of the compound to the magnetic field. In this case, the ME effect arises due to the stress-mediated contribution.

Performations investigations reveal the existence of a certain coupling between ferroelectricity and magnetism in the paramagnetic state of DMAGaS:Cr crystal. The existence of the ME effect in the paramagnetic state looks unusual, and there are very few known examples so far. The first of them concerns NiSO$_4 \times$ 6H$_2$O paramagnetic crystal [52]. The authors of this publication even termed the magnetoelectric coupling observed in this compound as paramagnetoelastic (PME) effect. According to their explanation, the ME coupling may appear in other piezoelectric paramagnetic crystals where the PME effect at low temperature is dominated by the variation of crystal field splitting D with the electric field. A similar effect was also observed in the ferroelectric–ferroelastic and simultaneously paramagnetic phase of Tb$_2$(MoO$_4$)$_3$ and Gd$_2$(MoO$_4$)$_3$ crystals [53]. The magnetoelectric effect was ascribed to the magnetostriction connected with Tb$^{3+}$ and Gd$^{3+}$ ions, along with the piezoelectric effect of the ferroelectric substance.

The magnetoelectric coupling observed in the organic–inorganic ferroics also would be associated with the effect of magnetostriction. The situation with the ME effect in DMAGaS:Cr crystal looks very similar to those in another representative of this family—[(CH$_3$)$_2$NH]Mn(HCOO)$_2$, which also would be related to the metal-organic frameworks (MOFs) [14]. Indeed, similarly to the case of DMAGaS:Cr crystal, the ferroelectricity in this MOF arises due to the ordering of DMA cations linked to other structural groups by the hydrogen bonds [14]. As it follows from the investigations of the magnetic susceptibility and ESR data the monoclinic crystalline structure of this compound favors the short–range superexchange interaction between Mn$^{2+}$ ions than the rhombohedral structure due to the modification in the Mn–Mn distance and angle. Such a correlation between the exchange interaction and lattice distortion has to be considered as magnetostriiction. Other proofs of certain ME coupling in the compounds of the MOF family were revealed by resonant ultrasound spectroscopy in [54].

Besides, very similar nature of the ME effect was suggested for DMAAl$_{1-x}$Cr$_x$S crystals [39]. It is known that DMAGaS:Cr crystal is characterized by the same nature of the ferroelectric ordering processes. Under such circumstances, by analogy with the case of DMAAl$_{1-x}$Cr$_x$S and [(CH$_3$)$_2$NH]Mn(HCOO)$_2$ MOF, one can conclude that the balance between superexchange and elastic energy causes the local distortion. The latter modifies the H–bonds and, respectively, the ordering of DMA groups, responsible for arising of spontaneous polarization. The applied magnetic field changes Cr–Cr distances, modifies the hydrogen bonds and process of DMA group order, and thus affects the spontaneous polarization. In comparison with the conventional ME effect in a magnetically ordered phase, these local magnetoelastic interactions in the paramagnetic state have to be weaker. Nevertheless, in the vicinity of the Curie point, the system of the ordering dipoles is very sensitive to internal influences, including the magnetic field. Under such circumstances, the strength of ME coupling in the vicinity of an order–disorder type PT should be high enough, as was observed in our experiments.

It is also necessary to note that the ME effect within the ferroelectric phase in DMAGaS:Cr is generally weaker than in DMAAl$_{1-x}$Cr$_x$S [38, 39]. First of all, this is caused by a lower concentration of chromium in DMAGaS:Cr. On the other hand, it is necessary to bear in mind a more considerable difference in the ionic radii in pairs Al$^{3+}$ and Cr$^{3+}$ from one side and Ga$^{3+}$ and Cr$^{3+}$ from the other ($R_{Mn} = 0.675 \text{Å}; R_{Ga} = 0.755 \text{Å}; R_{Ga} = 0.760 \text{Å})$ [55]. Under such circumstances, the local lattice deformations arising at the substitution of gallium with chromium should be much less than in the case of aluminum substitution with chromium. As a result, the effect of magnetostriction as well the ME coupling should be less pronounced in DMAGaS:Cr.

The proposed model based on the arising of the local lattice deformations could also be used for the explanation of the nontrivial magnetic–field dependence of the spontaneous polarization. Indeed, the substitution of Ga$^{3+}$ with Cr$^{3+}$ is followed by the local lattice deformations that cause the arising of the local polarization due to the piezoelectric effect. The magnetic field through the magnetostriction effect changes the level of the local lattice deformations, and consequently, the polarization [39].

The complicated mechanism of dipole ordering would explain the observed nonlinear dependences of the polarization change on the magnetic field. It is necessary to note that the ferroelectric PTFs both in the initial DMAGaS and DMAGaS:Cr are connected with the ordering of the polar DMA groups [40–42, 56]. According to reference [55], DMA cations in DMAGaS have to be related to two sublattices (the elementary cell consists of two nonequivalent groups). The orientation of these DMA groups is characterized by four possible localizations of N atoms belonging to these groups in the XZ plane projection (denoted by the numbers 1–4). It was shown by authors of [55], that the ferroelectric ordering of DMA groups between the 1–2 position axis is followed by the
antiferroelectric ordering along the 3–4 axis and vice versa. DMAGaS:Cr crystals are expected to be characterized by a similar scheme of DMA cation ordering. One can suggest that the magnetic field would affect the process of dipole ordering via the influence on the local lattice deformation connected with introducing the chromium ion instead of gallium. Considering that the magnetic field was directed along the ferroelectric axis, its impact on the ordering in these two different sublattices will be different, including even the sign of the corresponding effect. The additional local polarizations of a different signs arising in both cases have to compete with each other. Under such circumstances, their sum would nonlinearly depend on the magnetic field. The proposed model of ME coupling fairly well correlates with the conclusions made on the basis of our EPR study. Nevertheless, the described complicated mechanism demands further study by the independent methods, for example, by XRD or high-resolution TEM which would be sensitive to the coupling of the magnetic field with the mentioned local lattice distortions.

4. Conclusion

This paper reported the creation of the paramagnetic moments in the initially diamagnetic DMAGaS crystal using the partial isomorphous substitution of Ga\(^{3+}\) ion with Cr\(^{3+}\). In addition, the specific heat investigations revealed clear evidence of a series of phase transitions related to different electric dipoles ordering. The different types of this ordering in the structure of DMAGaS:Cr were evidenced in the temperature dependence of the magnetic moment and the evolution of the EPR spectra. A considerable ME coupling was demonstrated within the paramagnetic and simultaneously ferroelectric phase of DMAGaS:Cr crystal. Indeed, the substitution of Ga\(^{3+}\) with Cr\(^{3+}\) causes the local lattice distortions, and the latter lead to arising of the local polarization due to the piezoelectric effect. The external magnetic field through the magnetostriction effect changes the level of the local lattice deformations caused by metal ion substitution. In fact, the applied magnetic field changes Cr-Cr distances and modifies the hydrogen bonds and process of DMA group ordering, affecting spontaneous polarization. Such a model is confirmed by the fact that the ME effect within the ferroelectric phase in DMAGaS:Cr is generally weaker than in DMAAl\(_{1-x}\)Cr\(_x\)S. This is caused not only by a lower concentration of chromium in the first compound but also by a more considerable difference in the ionic radii between Al\(^{3+}\) and Cr\(^{3+}\) than between Ga\(^{3+}\) and Cr\(^{3+}\). Under such circumstances, the local lattice deformations arising at the substitution of gallium with chromium should be much less than in the case of aluminum substitution with chromium. As a result, the effect of magnetostriction and the ME coupling should be less pronounced in DMAGaS:Cr.

On the other hand, in the narrow temperature range in the vicinity of the Curie point, DMAGaS:Cr crystals are characterized by the largest values of the coefficient of ME interaction as well as the largest magnetodielectric effect within the family of ferroics with an organic cation including those in DMAAl\(_{1-x}\)Cr\(_x\)S. The observed maximum of \(\alpha_{\text{ME}}\) arises due to the shift of the I order PT under the action of the applied magnetic field and the coexistence of two phases in the vicinity of \(T_{c1}\), respectively. Finally, one can conclude that solid solutions of \(\text{NH}_2(\text{CH}_3)_2\text{Me}_1-x\text{Cr}_x(\text{SO}_4)_2 \times 6\text{H}_2\text{O}\) type with \(\text{Me} = \text{Al, Ga}\) would be considered a new family of effective magnetodielectric materials. The example of these materials demonstrates that it is possible to generate a large ME coupling and even tune its sign and strength using the partial isomorphous substitution of Me ion with chromium.

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Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.

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