

Temperature dependence of the antiferromagnetic order in CeCrO_3

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Among the orthochromites comprising a magnetic rare-earth constituent, CeCrO_3 exhibits the highest Néel temperature of ~ 260 K. Using high-resolution neutron powder diffraction, we redetermined the low-temperature antiferromagnetic Cr and Ce magnetic moment configuration in CeCrO_3 . The Cr moments order with a weakly canted G -type antiferromagnetic structure (Γ_2) where the moments essentially align along the b axis ($Pnma$ setting of the space group No. 62). Very weak Ce magnetic coherent scattering appears below ~ 22 K due to a C_x -type ordering of the Ce moments ($\mu_{\text{Ce}} \approx 0.06 \mu_B$). From the temperature dependence of the lattice parameters, we analyze the volume magnetoelastic effects which cause a contraction of the cell volume on ordering of the Cr moments. Below ~ 150 K a subtle but continuous adjustment of the a and c lattice parameters takes place which is attributed to a spin reorientation of the Cr magnetic moments. The temperature dependence of the Cr magnetic order parameter indicates a gap in the magnon spectrum. We reanalyze the specific heat capacity of CeCrO_3 which at low temperatures exhibits additional contributions due to thermal excitation within the crystal-field split levels of the $\text{Ce}^{3+} {}^2F_{5/2}$ Hund's rule ground state. A model calculation of the magnetization including magnetic polarization of the Ce moments is consistent with a spin reorientation of the Cr magnetic moments.

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I. INTRODUCTION

Rare-earth (R) orthochromites with composition $R\text{CrO}_3$ ($R = \text{Y, La - Lu}$) crystallizing with the distorted perovskite GdFeO_3 crystal structure type (see Fig. 1) have lately attracted particular attention because of their compelling magnetic, dielectric, magnetocaloric, gas sensing, and catalytic properties [1–4]. In the crystal structure of the $R\text{CrO}_3$ compounds, the Cr cations are coordinated by six oxygen anions in a distorted octahedral coordination shell. Within the a - c plane (space group No. 62 $Pnma$ setting), the Cr cations are connected via O2 anions in their equatorial planes with Cr-O2-Cr bonding angles amounting to $\sim 155^\circ$. Along the crystallographic b axis the Cr atoms connect via apical O1 anions with bonding angles comparable to those found via the O2 anions. The R cations are eightfold oxygen coordinated and reside in a strongly distorted antiprismatic oxygen coordination shell. Generally, in the $R\text{CrO}_3$ systems the Cr^{3+} magnetic moments exhibit antiferromagnetic (AFM) order with Néel temperatures T_{N1}

between room temperature (LaCrO_3) and ~ 110 K (LuCrO_3), often with the development of a weak ferromagnetic (FM) moment. By increasing the number of $4f$ electrons, i.e., by reducing the ionic radii of the R^{3+} cations and concomitantly the cell volume the T_{N1} 's decrease monotonously (see Fig. 2) [5].

Of special interest due to the intricate but crucial role of the Cr- R and R - R exchange coupling is the magnetism of the R atoms. The AFM ordering temperatures T_{N2} of the R moments (see inset to Fig. 2) are fairly low. Except for the two Kramers-ion systems, Nd^{3+} and Er^{3+} , the T_{N2} s are smaller than 5 K. A proportionality of T_{N2} to the total angular momentum of the Hund's rule ground-state total angular momentum J of the R^{3+} cations is not observed, indicating a critical influence of the details of the Cr magnetic ordering configuration, including possible spin canting, but also pointing to the importance of crystal-electric-field (CEF) splitting effects.

Still controversially discussed and closely connected to crystal structure details like, e.g., distorted oxygen coordination shells or exchange-striction effects is the origin of ferroelectricity and magnetoelectric effects observed in a number of the $R\text{CrO}_3$ systems [1–3,8,9]. Also, magnetocaloric properties connected to the AFM transitions of the Cr moments, especially of the orthochromites of the heavier R elements, are a matter of ongoing interest [3,10–12].

Employing neutron powder diffraction (NPD) a first investigation into the magnetic ordering configurations of the Cr moments in a $R\text{CrO}_3$ system was carried out very early on by Koehler and Wollan on LaCrO_3 [13]. Subsequently, using NPD and symmetry analyses the antiferromagnetic structures of the Cr and the R moments of a number of the $R\text{CrO}_3$

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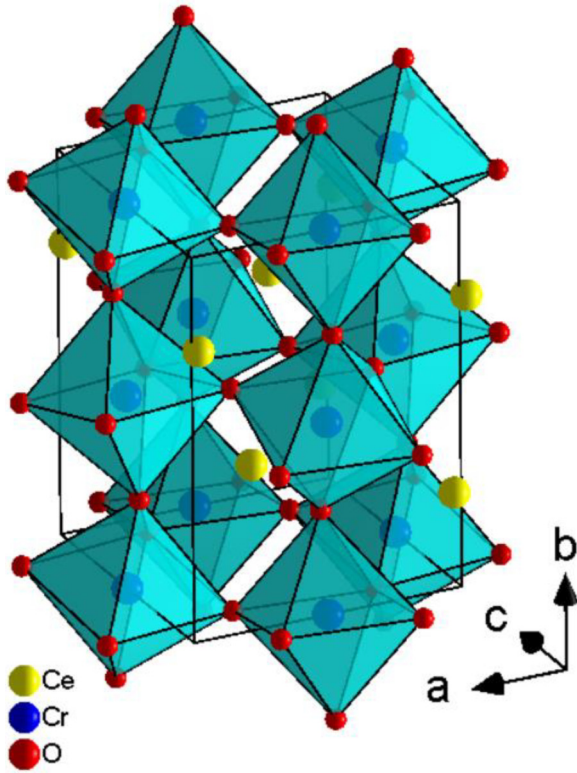


FIG. 1. Crystal structure of CeCrO_3 (space group No. 62 $Pnma$ setting).

compounds were determined by Bertaut and collaborators [14–17]. They studied in detail the symmetry-compatible magnetic configurations of the Cr and R magnetic moments and showed that three out of four symmetry-allowed magnetic symmetry modes grant canting of the Cr moments and a weak ferromagnetic (FM) moment.

In an early review, Hornreich summarized the ordering patterns of the $R\text{CrO}_3$ systems [18]. Prominently, two irreducible representations (Γ_4 , and Γ_2 , and rarely Γ_1 are met in the Cr AFM configurations [14,19]. Some of the $R\text{CrO}_3$ compounds showing a Γ_4 AFM configuration immediately below T_{N1} start to undergo a spin-reorientation transition in which they transform to a Γ_2 magnetic configuration at low temperatures. Those $R\text{CrO}_3$ compounds starting with a Γ_2 magnetic structure appear to remain with the Γ_2 configuration, however, some of them pass through a compensation of Cr and R magnetic moments.

Lately, the magnetic ordering properties of the $R\text{CrO}_3$ have attracted renewed attention due to improvements in NPD techniques. One example highlighting the complex magnetic behavior of the $R\text{CrO}_3$ compounds is SmCrO_3 . As recently described by Sau *et al.* and Klingeler *et al.*, SmCrO_3 orders with a Γ_4 (G_x , A_y , F_z in $Pbnm$ setting) magnetic structure below T_{N1} , and in a continuous spin reorientation passes to a Γ_2 (F_x , C_y , G_z) magnetic configuration below 37 K. At even lower temperature a spin configuration with polar order is proposed [20,21]. A recent NPD investigation revealed a similarly complex low-temperature magnetic behavior of GdCrO_3 [22]. Consistent with early magnetization measurements [23] a Cr spin reorientation from Γ_4 to Γ_2 takes place at about

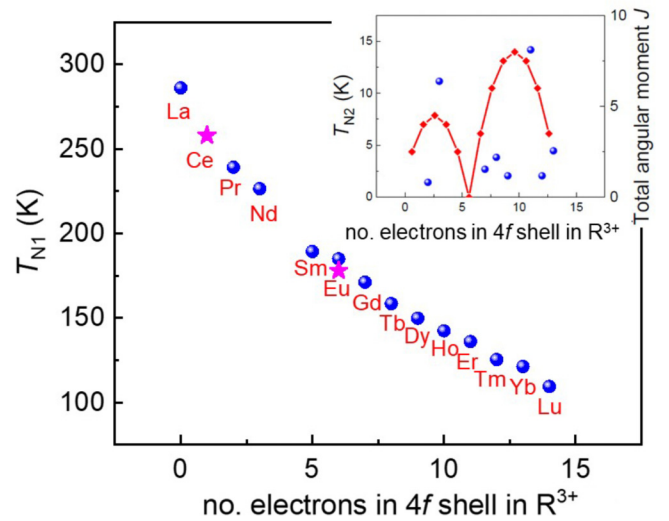


FIG. 2. (Blue dots) Antiferromagnetic ordering temperature T_{N1} of the Cr magnetic moments and magnetic ordering temperature T_{N2} (blue dots inset) of the R moments (inset) as a function of the number of electrons in the $4f$ electron shell. Main frame: Blue dots were taken from Prado *et al.* [5]; magenta asterisks are obtained from Taheri *et al.* [6,7]. Red dots in the upper inset represent the total angular momentum J of the particular R^{3+} cation (right ordinate), the solid line is a guide to the eye.

8 K which, however, remains incomplete and a continuing repercussion of the Cr sublattice on the Gd magnetism takes place. Below 2.3 K an incommensurate polar phase exists, connected to Gd magnetic ordering [22].

Often, the low-temperature magnetic order of the $R\text{CrO}_3$ is very sensible to external magnetic fields or pressure. A magnetic-field-induced reorientation of the spin canting and the weak FM component had early on been generated for ErCrO_3 [24]. Switching of the weak FM component already by moderate magnetic fields or low pressure has lately been reported for GdCrO_3 and $\text{Gd}_{1-x}\text{Y}_x\text{CrO}_3$ [25–27]. Another $R\text{CrO}_3$ system where such magnetization reversal at low temperatures can be initiated by external magnetic fields already of the order of 1 kOe is CeCrO_3 [6,28–30].

These effects reflect the complex interplay of the Cr and R magnetism. However, the magnetic ordering configurations of the Cr and R moments have not been conclusively established for all members of the $R\text{CrO}_3$ series. Two systems that were not covered by the earlier investigations were EuCrO_3 and CeCrO_3 . Aside from the high-absorption cross section for thermal neutrons of the natural composition of Eu isotopes, Eu^{3+} magnetism in EuCrO_3 is particularly difficult to ascertain because of the energetically close 7F_n ($n = 0, \dots, 7$) CEF levels which leave the magnetic moment markedly temperature dependent. In a recent paper, we have analyzed the AFM ordering pattern of EuCrO_3 and also suggested a canting pattern of the Cr magnetic moments [7]. Another $R\text{CrO}_3$, the magnetic properties and especially the magnetic structure of which are currently discussed, is CeCrO_3 . CeCrO_3 exhibits several peculiarities: AFM of the Cr magnetic moments in CeCrO_3 takes place shortly below room temperature at ~ 260 K and thus shows the highest Néel temperature T_{N1} of all magnetic R elements in the $R\text{CrO}_3$ compounds [5]. Aside

from a complex magnetization behavior with a magnetization compensation at ~ 120 K, relaxorlike dielectric behavior ascribed to polar nanodomains has been observed [6,28–30]. Whereas for all other $RCrO_3$, especially for the heavier rare earth, the lattice parameters a and b ($Pnma$ setting of space group No. 62 [31]) are distinctly different, they are almost identical for $CeCrO_3$, i.e., metrically $CeCrO_3$ approaches tetragonal symmetry (see, e.g., Fig. 5 in Ref. [30]).

Shukla *et al.* reported a collinear G -type Cr magnetic structure for $CeCrO_3$ at 22 K with the Cr magnetic moments in the plane perpendicular to the long $7.73\text{-}\text{\AA}$ c axis corresponding to the Γ_1 configuration) and also ordering of the Ce magnetic moments. They refined a Ce-ordered magnetic moment of $0.7\text{ }\mu_B$, aligned as well perpendicular to the long axis [28]. By comparing neutron powder diffraction and magnetization data, Yadav *et al.* recently proposed a spin-reorientation transition of the Cr magnetic moments from a magnetic structure described by the irreducible representation Γ_4 to Γ_2 , however, they concluded that it is challenging to verify a conclusive magnetic configuration based on the fitting of NPD data [32].

Here, we report on an in-detail reinvestigation of the magnetic properties especially of the magnetic structure of $CeCrO_3$ using high-resolution NPD measurements. Adverse to the preceding report by Shukla *et al.*, we find a different orientation of the Cr moments with the main component pointing along the long b axis and a very weak additional AFM component ($\sim 0.02\text{ }\mu_B$) along the a axis (Γ_2 irreducible representation, configuration C_x, G_y, F_z). Below ~ 22 K the Ce magnetic moments order with a C -type coupling (C_x) and very small ($\sim 0.06\text{ }\mu_B$) moments being essentially perpendicular to the Cr magnetic moments. With a detailed analysis of a series of temperature-dependent NPD patterns we analyze thermal and magnetoelastic effects on the crystal structure of $CeCrO_3$. By analyzing specific heat capacity data, we find a CEF level scheme of the $^2F_{5/2}$ Hund's rule ground state of Ce^{3+} which we use in a model calculation to investigate the spin reorientation of the Cr magnetic moments.

II. EXPERIMENT

A large powder sample of $CeCrO_3$ suitable for NPD was prepared by the combustion method followed by subsequent annealing as described in detail previously [6,33]. Phase purity of the samples was checked by x-ray powder diffraction (XRPD) with a D8 advance powder diffractometer (Bruker, Germany) using $MoK_{\alpha 1}$ and $CuK_{\alpha 1}$ radiation.

Crystals for the heat capacity measurements were grown in an optical floating zone (OFZ) furnace. In order to enable a compact pressing of rods suitable for OFZ growing the sample used for NPD was ball milled, transferred to an alumina crucible, and heated to 800°C for 24 h to reduce the crystallinity. After ball milling of the sintered powder again cylindrically shaped feed and seed rods were prepared by filling the powder into rubber tubes (6 mm diameter), which were evacuated and compacted in a stainless steel form filled with water using a Riken-type S1-120 70 kN press. Subsequently, the rods were heat treated at 800°C . Single-crystal growth was carried out in a high-temperature optical floating zone furnace (model Crystal Systems Xenon OFZ), which allows for temperatures up to 3000°C . The system is equipped with four xenon lamps

operating at 1 kW in a horizontal mirror alignment. The seed rods were aligned in the furnace and for a first growth run the chamber was pressurized with 3 bar argon gas held at a flow rate of 1 l/min. Due to the expected evaporation a gas guide (narrow quartz glass tube from Crystal Systems) was used as a cold trap for the evaporated material. After establishing a proper molten liquid at 50% lamp power, we connected the molten zone, and the growth was carried out by moving the seed with a speed of 18 mm/h and the feed was moved with 23 mm/h. During growth the lamp power was reduced to 43%. After 2 cm of growth we reduced the seed speed to 10 mm/h, which required an increase in power. Elevated evaporation from longer period in the molten zone necessitated an augmentation of the feed to 20 mm/h. This resulted in a successful grain selection after 2 cm of growth, with the main grain oriented with an angle of about 20° . The final 3 cm of the seed rod were fed forward with a speed of 18 mm/h and 23 mm/h. Finally, we broke the polycrystalline seed and used it as a new feed and oriented the seed vertical and continued growth with the same conditions resulting in a total 9-cm boule. Since the only stable phases are $CeCrO_3$, Ce_2O_3 , and Cr_2O_3 , the evaporated Cr_2O_3 was balanced by Ce_2O_3 crystals formed on the surface of the boule. By energy-dispersive x-ray spectroscopy (EDX) we confirmed the correct stoichiometric of the single crystals.

NPD patterns were collected on a ~ 20 -g sample using Institut Laue-Langevin's (ILL's) (Grenoble, France) D2B high-resolution powder diffractometer for thermal neutrons with neutrons of wavelengths of 1.594 and $2.39851\text{ }\text{\AA}$ [34]. The thermal dependence of the diffraction pattern (thermodiffractogram) was measured between 1.5 and 309 K using ILL's high-intensity powder diffractometer D20 with neutrons at a wavelength of $2.424\text{ }\text{\AA}$ [35]. Patterns were recorded every 10 min while changing the temperature by 0.1 K every 30 s resulting in a temperature resolution of 2 K. Additional data sets with very high statistics were taken at 1.5 , 10 , 22 , 30 , 60 , 100 , 125 , and 300 K measuring each temperature for $5\text{--}6$ h. Rietveld profile refinements of the diffraction patterns were performed with the fullprof software package [36]. The specific heat capacities of a crystalline piece (10.5 mg) of $CeCrO_3$ were measured as a function of temperature in a Physical Property Measurement System system (PPMS, Quantum Design) employing the relaxation method.

III. RESULTS

A. Crystal structure

Figure 3 displays a NPD ($\lambda = 1.594\text{ }\text{\AA}$) and an x-ray powder diffraction (XRPD) pattern ($CuK_{\alpha 1}$) collected on our sample at room temperature. A Rietveld profile refinement of the patterns confirmed the orthorhombic crystal structure of $CeCrO_3$ and did not reveal additional Bragg peaks from impurity phases. Table I lists characteristic structural parameters for $CeCrO_3$ obtained from Rietveld profile refinements of high-intensity powder patterns collected on ILL's high-resolution two-axis diffractometer D2B for four selected temperatures. Tables II and III summarize characteristic interatomic distances and angles as a function of temperature.

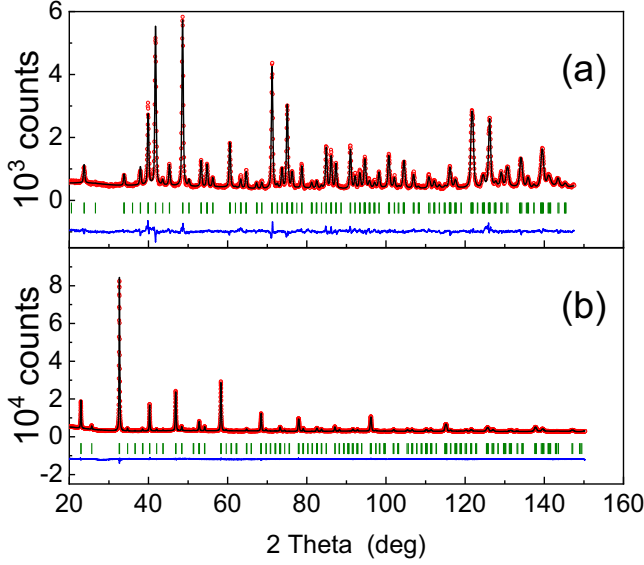


FIG. 3. (a) Neutron powder diffraction pattern ($\lambda = 1.594$ Å) and (b) an XRPD pattern ($\lambda = 1.5406$ Å) of our polycrystalline sample of CeCrO_3 collected at 300 K. The red circles display the measured, the black solid lines represent the patterns calculated using the positions of the Bragg angles indicated by the green vertical bars below. The blue solid lines show the difference between measured and calculated patterns.

TABLE I. Structural parameters of CeCrO_3 obtained from Rietveld profile refinements of the NPD patterns collected on ILL's diffractometer D2B (high-intensity mode) at the indicated temperatures using neutrons of a wavelength of $\lambda = 1.594$ Å. The Rietveld refinements were performed assuming the space group $Pnma$ (No. 62). Positional parameters which are not listed in the table are $\equiv 0$. Refinement of the occupancies of the oxygen atoms O1 and O1 converged to full occupancy.

T (K)	300	120	5	1.6
a (Å)	5.47971(23)	5.47369(13)	5.47620(14)	5.47584(7)
b (Å)	7.74086(30)	7.72353(17)	7.72333(16)	7.72439(8)
c (Å)	5.48768(21)	5.48098(17)	5.48097(14)	5.48322(7)
V (Å ³)	232.774(16)	231.715(9)	231.816(9)	231.926(5)
Ce (4c)				
x	0.5287(6)	0.5281(5)	0.5297(4)	0.5302(7)
y	0.25	0.25	0.25	0.25
z	0.5069(9)	0.5040(8)	0.5044(6)	0.5045(9)
Cr (4b)				
x	0.5	0.5	0.5	0.5
O1 (4c)				
x	-0.0104(6)	-0.0110(5)	-0.0113(5)	-0.0123(7)
z	0.4297(6)	0.4280(5)	0.4255(4)	0.4229(5)
O2 (8d)				
x	0.2823(3)	0.2820(3)	0.2813(3)	0.2821(5)
y	0.0386(2)	0.0389(2)	0.0378(2)	0.0378(2)
z	0.7156(5)	0.7163(3)	0.7159(3)	0.7164(5)
m_0 (μ_B)		2.33(2)	2.40(2)	2.54(2)
λ (Å)	1.594	1.594	1.594	2.39851
R_p (%)	4.75	4.96	4.09	2.80
R_F (%)	4.15	4.06	2.78	1.55
R_{mag} (%)		2.10	1.55	1.62

TABLE II. Characteristic interatomic Ce-Cr distances for CeCrO_3 calculated from the data listed in Table I.

	300 K	120 K	5 K	1.6 K
d (Ce-Cr) (Å)				
(2 ×)	3.227(3)	3.225(2)	3.219(2)	3.217(3)
(2 ×)	3.333(4)	3.338(4)	3.337(4)	3.337(4)
(2 ×)	3.390(5)	3.374(4)	3.375(4)	3.378(4)
(2 ×)	3.484(3)	3.476(4)	3.484(4)	3.487(3)

The temperature dependence of the lattice parameters and the atom positional parameters gained from a sequence of neutron powder diffraction measurements are summarized in the Supplemental Material where also a comparison with literature data and a detailed Debye fit are discussed [37–39].

B. Neutron diffraction

1. Critical behavior and T_{N1}

Between 1.5 and 309 K a set of neutron powder diffraction patterns was collected as a function of temperature on ILL's high-intensity medium-resolution diffractometer D20 using neutrons of the wavelength of 2.424 Å (see Fig. 4). Extra Bragg peaks at $d = 4.46$ Å and extra intensity at $d = 3.85$ Å, apparently of magnetic origin, appeared below ~ 260 K. The magnetic peaks could be indexed on the basis of a magnetic propagation vector $\vec{k} = (0, 0, 0)$. In order to ascertain the critical temperature T_{N1} and the critical exponent β of the sublattice magnetization, the strongest magnetic Bragg peak indexed as (1,1,0) was fitted with a Gaussian. Figure 5 displays the integrated intensity as a function of temperature

TABLE III. Characteristic interatomic Cr-O1/O2-Ce angles for CeCrO_3 calculated from the data listed in Table I.

	300 K	120 K	5 K	1.6 K
$\angle$ (Cr-O -Cr) (deg)				
(2 ×)	157.21(16)	156.64(16)	155.85(13)	157.31(16)
$\angle$ (Cr- O2-Cr) (deg)				
(2 ×)	156.96(11)	157.02(16)	157.43(10)	157.39(13)
$\angle$ (Cr-O1-Ce) (deg)				
(2 ×)	78.64(8)	78.36(8)	77.96(7)	78.71(8)
(2 ×)	86.77(10)	86.66(10)	86.51(9)	86.51(12)
(2 ×)	89.71(11)	89.86(11)	89.76(9)	90.10(12)
(2 ×)	101.07(9)	101.34(9)	101.71(7)	100.93(8)
$\angle$ (Cr-O2-Ce) (deg)				
(2 ×)	77.2(5)	77.0(5)	77.18(8)	77.26(11)
(2 ×)	79.9(5)	80.1(5)	80.34(8)	80.11(11)
(2 ×)	84.6(6)	84.7(6)	84.83(9)	84.53(12)
(2 ×)	87.5(5)	87.4(5)	87.17(10)	87.41(14)
(2 ×)	90.0(5)	89.7(5)	89.91(10)	90.30(13)
(2 ×)	91.6(6)	91.8(6)	91.88(10)	91.64(14)
(2 ×)	98.0(6)	98.3(6)	97.81(11)	97.72(15)
(2 ×)	104.9(6)	104.6(6)	104.62(11)	104.76(15)

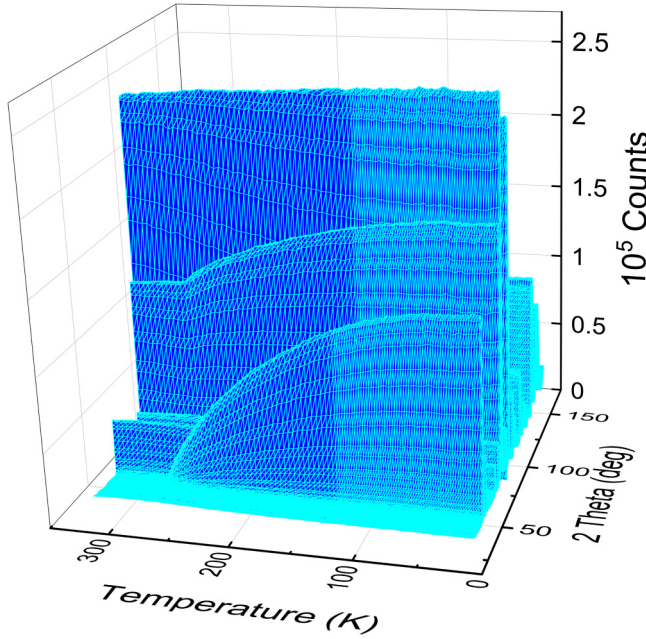


FIG. 4. Temperature dependence of a series of NPD patterns (thermodiffractogram) collected at ILL's high-intensity medium resolution diffractometer D20 between 1.5 and 309 K with neutrons of a wavelength of 2.424 Å.

which fits well to a power law according to

$$I(T) = I_0 t^{2\beta}, \quad (1)$$

where the reduced temperature t is given by $(T_{N1} - T)/T_{N1}$. The fit indicates a critical temperature T_{N1} of the Cr magnetic

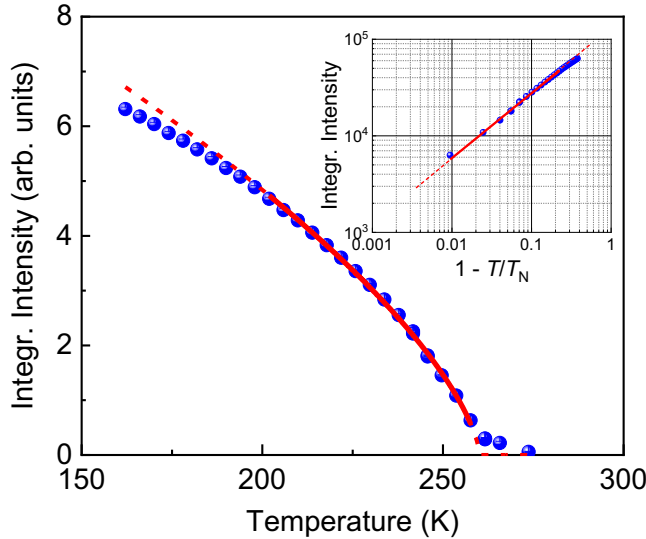


FIG. 5. Integrated intensity of the (1,1,0) magnetic Bragg reflections as function of temperature. The solid red line shows a fit of the intensities with a power law [Eq. (1)] resulting in critical parameters given in the text. The upper inset displays a log-log plot of the integrated intensities as a function of the reduced temperature with a critical exponent $\beta = 0.34$.

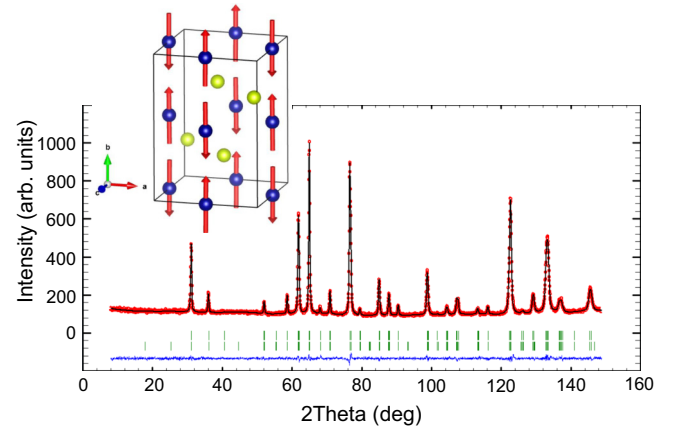


FIG. 6. Neutron powder diffraction pattern of our polycrystalline sample of CeCrO₃ collected at 1.6 K on ILL's high-resolution powder diffractometer D2B using neutrons of a wavelength of 2.3985 Å, $R_{\text{Bragg}} = 1.9$, $R_{\text{mag}} = 1.6$, $\chi^2 = 1.6$. The red circles display the measured, the black solid line represents the pattern calculated using the positions of the Bragg angles indicated by the green vertical bars. The blue solid line below highlights the difference between measured and calculated patterns. The inset displays the arrangement of the Cr magnetic moments with $\mu_{\text{Cr}} = 2.54 \mu_B \parallel b$ (G_y configuration of Γ_2).

moments of

$$T_{N1} = 260.0(5) \text{ K},$$

and a critical exponent of

$$\beta = 0.34(3).$$

Given the limited number of data points, T_{N1} and β depend on the temperature interval chosen for the fits (see, e.g., Ref. [40]). The quoted error bars are an average of fit results including various temperature intervals between 200 and ~ 260 K. Néel temperature T_{N1} and critical exponent are close to what has been reported before [30]. The critical exponent is consistent with that of standard three-dimensional universality classes.

2. Cr moment order

Our magnetic structure solution is based on a NPD pattern collected for 24 h on D2B using the long wavelength of $\lambda = 2.3985$ Å and highest available resolution: The divergence of the primary neutron beam was reduced by a 10° collimator and the secondary neutron beam diffracted was additionally collimated by closing slits positioned behind the monochromator. For the propagation vector $\vec{k} = (0, 0, 0)$ a symmetry analysis employing the program basireps available in the fullprof program package [36] resulted in four irreducible representations for possible antiferromagnetic arrangements of the Cr atoms. A successful profile refinement proved a magnetic G -type antiferromagnetic structure with the Cr magnetic moments of $\sim 2.5(1) \mu_B$ being parallel to the b axis ($Pnma$ setting) corresponding to the Γ_2 (C_x , G_y , F_z) configuration (see Fig. 6). The refinements also indicated a possible very small $[0.1(1) \mu_B]$ FM moment along the c axis. However, given the error bar, we do not consider it tenable. Assuming

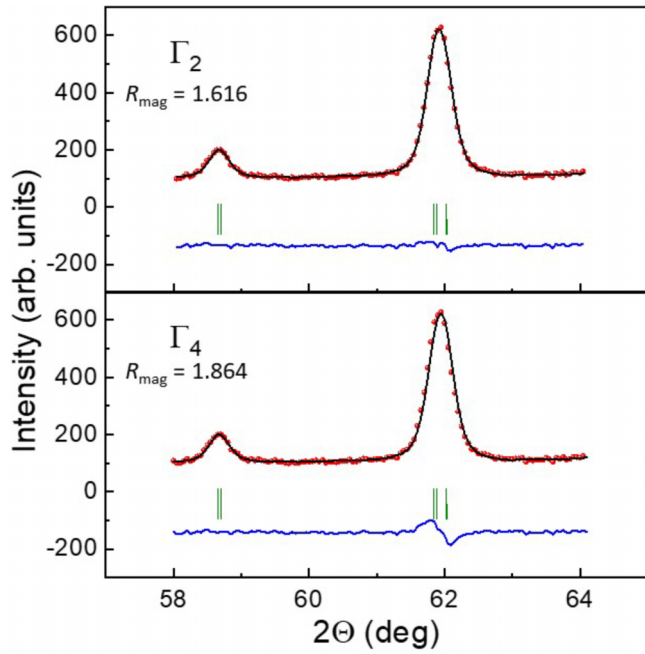


FIG. 7. Comparison of the Rietveld profile refinements between 58° and 64° of the neutron powder diffraction pattern collected at 1.6 K on ILL's high-resolution powder diffractometer D2B using neutrons of a wavelength of 2.3985 Å. The dominant reflection comprises magnetic scattering from the superposition of magnetic Bragg reflections 112/211 and 031/130. The red circles display the measured, the black solid line represents the pattern calculated using the positions of the Bragg angles indicated by the green vertical bars. The blue solid lines below highlight the differences between measured and calculated patterns.

a Γ_1 or a Γ_4 configuration with moments along the a axis, respectively c axis, returns profile refinements with somewhat increased R_{mag} values. The Γ_2 moment configuration is strongly supported by a closer comparison of the intensities of the 112/211 Bragg reflections with the 031/130 reflection group (61.8° (2Θ) 62.1°). By putting the Cr moments along b the intensities of the former are somewhat enhanced, resulting in an overall improved fit with a clearly reduced difference between measured and calculated patterns and a smaller R_{mag} value (see Fig. 7). Our magnetic structure solution is different to the results reported by Shukla *et al.* who found the Cr moments to align along b ($Pbnm$ setting), equivalent to a in our $Pnma$ setting [28]. In addition, a closer inspection of the difference between measured and calculated D2B patterns showed no clear extra features indicating long-range ordering of the Ce moments. This finding rules out a Ce moment of the order of $0.7\mu_B$ as concluded by Shukla *et al.* [28].

3. Cr spin canting and Ce moment order

In case of the isostructural compound CeFeO_3 it had been found that a first-order spin reorientation of the Cr moment from a Γ_4 to a Γ_1 configuration takes place at about 230 K before a very small ordered magnetic moment of about $0.11\mu_B$ appears on the Ce site below about 30 K [41]. This motivated us to search for possible additional components C_x or F_z in the Cr order [$\Gamma_2 = (C_x, G_y, F_z)$] which would lead to canting of

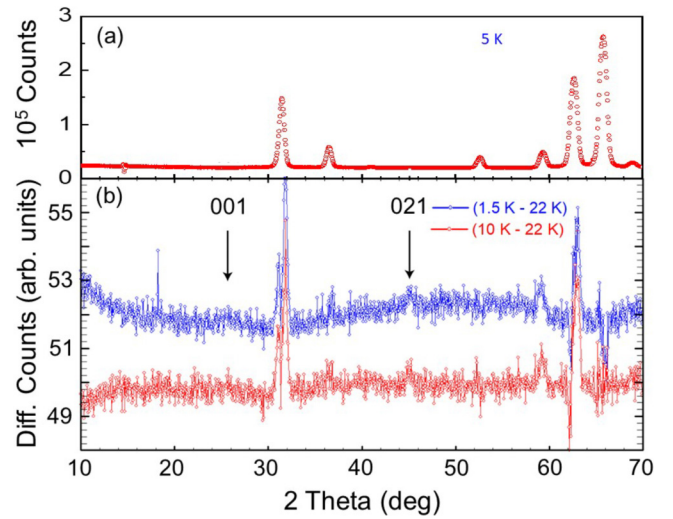


FIG. 8. (a) Neutron powder diffraction pattern of CeCrO_3 collected at 5 K at ILL's high-intensity powder diffractometer D20. (b) Smoothed difference patterns, 1.5–22 K and 10–22 K.

the spins away from the main direction and for a magnetic moment of the Ce atoms using our very long high-intensity D20 diffraction patterns. Below ~ 20 K, a small additional Bragg reflection appears at $2\Theta \approx 45^\circ$ ($d = 3.3$ Å) which is best seen in a smoothed difference plot 1.5–22 K. It can be indexed as (0 2 1) (see Fig. 8). An additional but less intense reflection (0 0 1) can be identified at $2\Theta \approx 25.5^\circ$ ($d = 5.6$ Å). These Bragg reflections can be captured by including an ordered magnetic moment on the Ce atoms [$\sim 0.06(1)\mu_B$] aligned along the crystallographic a axis, i.e., perpendicular to the dominant component of the Cr moments as highlighted in Fig. 9. The intensity imbalance of these two weak Bragg reflections can be taken care of by adding a small C -coupled moment on the Cr atoms [$\sim 0.02(1)\mu_B$] leading to a faint spin canting of the Cr moments out of the b direction, along the a axis which is allowed in the Γ_2 configuration (C_x, G_y, F_z). Given the very low intensity and the associated statistical uncertainties, especially of the (0 0 1) reflection, the above conclusions require further confirmation, e.g., by a single-crystal magnetic structure determination.

4. Magnetic diffuse scattering

In addition to coherent magnetic scattering below T_{N1} , the integrated intensities revealed pedestals at these Bragg positions for $T > T_{N1}$ which are assigned to critical magnetic scattering on approaching T_{N1} . A closer inspection of the diffuse intensities near T_{N1} at around the $d = 4.43$ Å [(1,1,0) magnetic reflection] revealed a weak broad bulge, the intensity of which peaks at $\sim T_{N1}$, but falls off rapidly for temperatures further away from T_{N1} . Figure 10 displays the diffuse scattering intensities relative to a pattern collected at 309.3 K as a function of temperature. The diffuse intensities fit well to a Lorentzian with rapidly decreasing full-width at half-maximum (FWHM) as T_{N1} is approached. A fit of the FWHM with a power law in the reduced temperature indicates a critical temperature of 258.0(5) K, close to the result obtained from the fit of the integrated intensities of

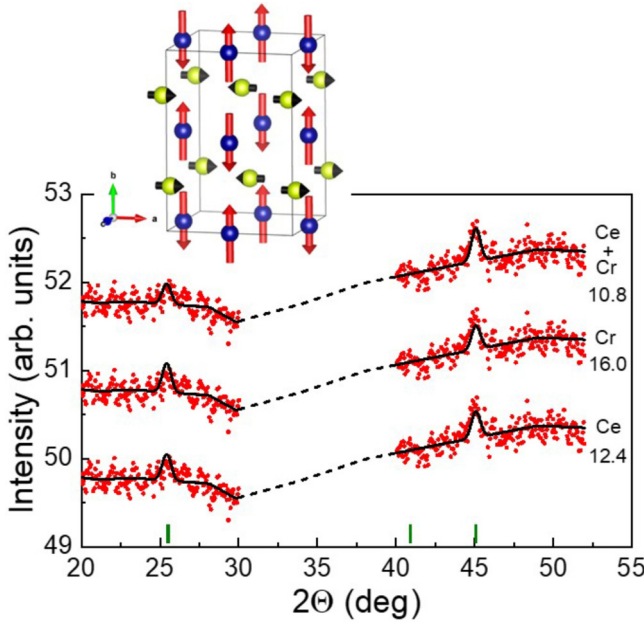


FIG. 9. Profile refinement of the Ce magnetic moment from a smoothed NPD difference pattern (D20: 1.5–22 K, see also Fig. 8). The three refinements correspond to models allowing a C_x component on both sublattices, only on the Cr sublattice, or only on the Ce site. Respective R_{mag} values are indicated. The inset displays the Cr and Ce magnetic moments, the latter aligned along the a axis ($Pnma$ setting). For better visibility the Ce moments ($\sim 0.06 \mu_B$) have been magnified by a factor of 20. Cr spin canting leading to a small additional AFM component is barely visible. The region between 30° and 34° has been excluded from the refinement.

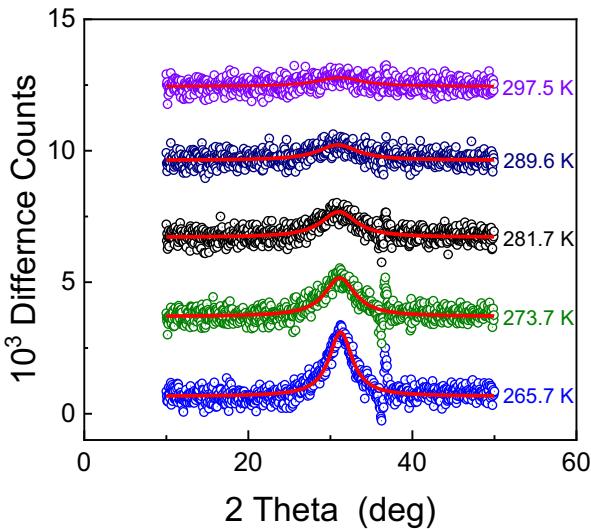


FIG. 10. Diffuse intensity observed at around $d = 4.46 \text{ \AA}$, i.e., the $(1,1,0)$ magnetic reflection for temperatures $T > T_{N1}$. The patterns were obtained by subtracting a background pattern collected at 309.3 K which showed no diffuse intensity any more. Each data set has been successively up-shifted by 3×10^3 counts. The solid red lines are fits to Lorentzians, the FWHM of which are displayed in FIG. 11. The spike at $\sim 48^\circ$ results from the incomplete subtraction of a strong nuclear reflection at this Bragg angle.

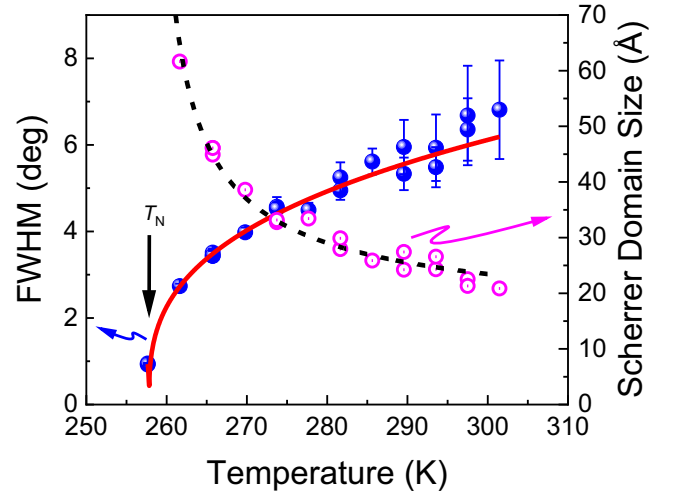


FIG. 11. (Blue dots) FWHM of the Lorentzians fitted to the diffuse difference intensity displayed in Fig. 10. The solid red line is a power law in the reduced temperature with $T_{N1} = 258.0(5) \text{ K}$. (Magenta circles) The average domain size calculated according to Scherrer's equation [Eq. (2)].

the principal magnetic Bragg reflection at $d = 4.46 \text{ \AA}$. The FWHM of the Lorentzian fitted to the diffuse peaks decreases towards T_{N1} indicating a growth of the magnetic domain size. We tentatively determined the average domain size $\tau(T)$ from the $\text{FWHM}(T)$ by using Scherrer's equation [42]

$$\tau = \frac{K\lambda}{\text{FWHM}'(T) \cdot \cos(\theta)}, \quad (2)$$

where $K \approx 0.9$ and $\text{FWHM}'(T)$ is the fitted $\text{FWHM}(T)$ corrected by the resolution of the diffractometer D20 ($\sim 0.65^\circ$ at $2\theta \sim 31^\circ$ [35]). The results summarized in Fig. 11 highlight that the average domain size diverges on approaching T_{N1} . At 300 K the average magnetic domain size still amounts to $\sim 20 \text{ \AA}$, corresponding to a domain volume comprising ~ 5 unit cells (see Table I).

5. Spin waves

The profile refinement of the temperature series of neutron powder diffraction patterns collected at the instrument D20 provides the temperature dependence of the Cr ordered magnet moment displayed as inset in Fig. 12. The decrease with temperature of the order parameter $M(0) - M(T)$, with respect to its fully saturated value, $M(T=0) = 2.54 \mu_B$, follows the square of the temperature, consistent with the expectation for an AFM with a gap in the spin-wave excitation spectrum. Following Kubo and Oguchi [43,44] the temperature dependence of the staggered magnetic moment in a simple cubic lattice is given by

$$M(T)/(g\mu_B) = \frac{N}{2} \left[S - \frac{1}{2}c' - \frac{\zeta(2)}{2\pi^2\eta^3} \left(1 - \frac{c}{S}\right) \Omega^2 \right], \quad (3)$$

wherein h , $c' = 0.156$ and $c = 0.097$ are constants taken from the work of Anderson [45], $\zeta(2)$ is Riemann's zeta function, spin $S = \frac{3}{2}$, and $\Omega = (k_B T)/(\hbar |J| S)$. For the number of nearest neighbors (NN) z we have used $z = 6$ at distances of $\sim 3.87 \text{ \AA}$, four Cr NN within the a - c plane and two along the b

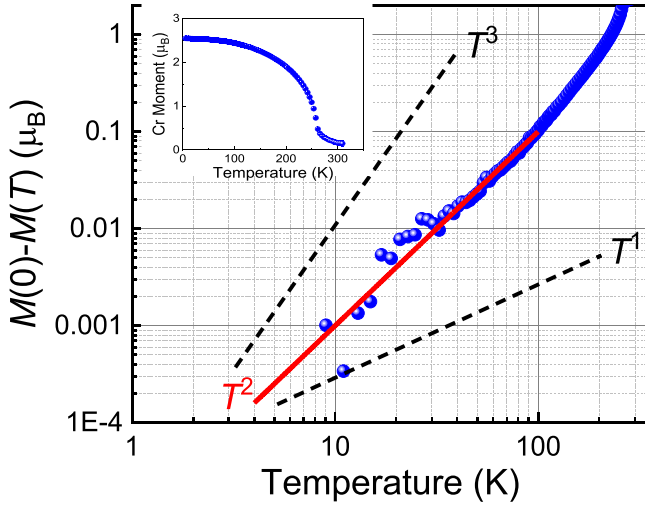


FIG. 12. Difference of the sublattice Cr magnetic moment, $M(T) - M(0)$, of CeCrO_3 as a function of the temperature. The red solid line represents a power law $M(T) - M(0) \propto 1.1(1) \times 10^{-5} T^2$. Linear and cubic power laws in T are represented by the black dashed lines as indicated. The upper inset shows the temperature dependence of the sublattice magnetization as obtained from the Rietveld profile refinements.

direction. We assumed as a first approximation that the Cr-Cr exchange constants are identical for the different neighbors following the result of the density functional theory (DFT) calculations by Zhu *et al.* [46]. By taking the experimentally determined coefficient of $1.1(1) \times 10^{-5} \text{ K}^{-2}$ (solid red line in Fig. 12) we arrive at an Cr-Cr exchange constant $|J| = 28(2) \text{ K}$. This value is in fair agreement with the exchange constant of $\sim 35 \text{ K}$ obtained by using Van Vleck's relation for T_{N1} [47],

$$T_{\text{N1}} = \frac{1}{3} \bar{z} 35 \text{ K } S(S+1) \approx 260 \text{ K}. \quad (4)$$

C. Specific heat capacity and magnetization

The neutron diffraction results and reported magnetization results of CeCrO_3 hint at a possible spin reorientation of Cr magnetic moments and a very small ordered Ce magnetic moment starting to develop essentially below about 20 K. Apart from polarization by the exchange fields imposed by the Cr moments, the Ce magnetism is also subject to CEF splitting of the $^2F_{5/2}$ Hund's rule ground state. In order to estimate the effect of CEF excitations to the heat capacity, we remeasured the specific heat capacity of CeCrO_3 in zero external magnetic field. The results obtained on a crystalline piece are shown in Fig. 13. The sharp λ anomaly at $258.0(0.5) \text{ K}$ marks the AFM ordering of the Cr magnetic moments, in good agreement with Néel temperatures T_{N1} found before [28,30]. Below $\sim 50 \text{ K}$ a bulge is visible which is attributed to the heat capacity contribution emerging from the Ce moments.

Without magnetic field the $^2F_{5/2}$ Hund's rule ground state will split into three Kramers doublets. The doublets may additionally split by exchange fields imposed by the Cr moments or an external magnetic field. In order to fit the heat capacity over the whole temperature range and to estimate the full CEF splitting, we have to take into account the lattice heat

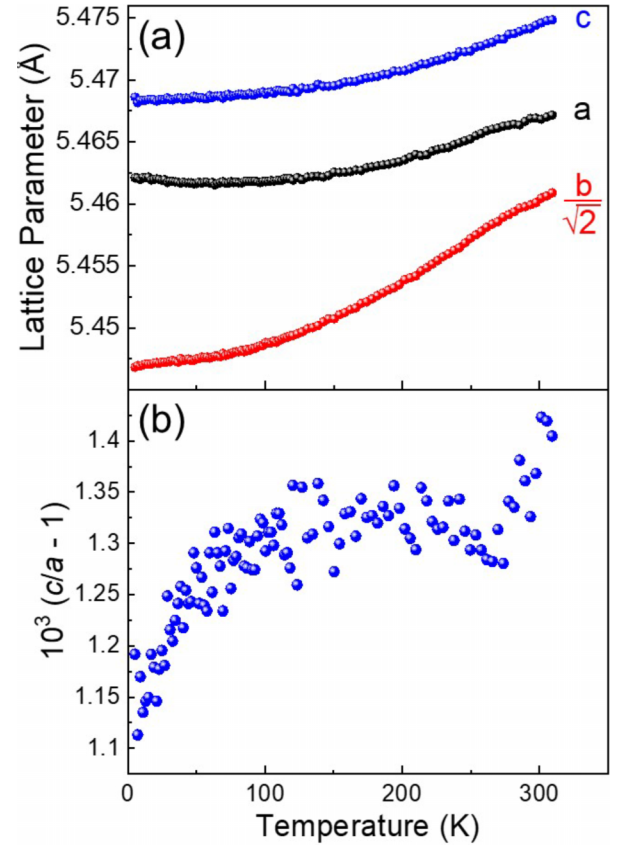


FIG. 13. (Blue dots) Specific heat capacity of CeCrO_3 . The upper inset highlights the temperature range around the AFM ordering of the Cr magnetic moments. The solid red line shows an estimate with a two-level Schottky heat capacity anomaly with a splitting of the levels of $\approx 50 \text{ K}$.

capacity as well which dominates the heat capacity at higher temperatures. To separate the magnetic contributions $C_{\text{mag}}(T)$ from the dominant lattice contribution C_{lat} , we therefore fitted the heat capacity between 2 and 225 K to a model adding both contributions according to

$$C_P(T) = C_{\text{mag}}(T) + C_{\text{lat}}(T), \quad (5)$$

where the lattice heat capacity $C_{\text{lat}}(T)$ was approximated by a superposition of a two Debye terms according to

$$C_{\text{lat}}(T) = n 9R \left(\sum_{i=1}^2 w_i \left(\frac{T}{T_{D_i}} \right)^3 \times \int_0^{T_{D_i}/T} \frac{x^4 \exp(T_{D_i}/T)}{[\exp(T_{D_i}/T) - 1]^2} dx \right), \quad (6)$$

where T_{D_i} are the Debye temperatures, R is the molar gas constant, and $n = 5$ the number of atoms in a formula unit. T_{D_i} and w_i are fitting parameters. For the Debye heat capacity we have used the Padé approximation given by Goetsch *et al.* [48].

The magnetic heat capacity $C_{\text{mag}}(T)$ of Ce^{3+} is given by

$$C_{\text{mag}}(T) = \frac{R}{(k_B T)^2} \frac{(\sum_i p_i)(\sum_i E_i^2 p_i) - (\sum_i E_i p_i)^2}{(\sum_i p_i)^2}, \quad (7)$$

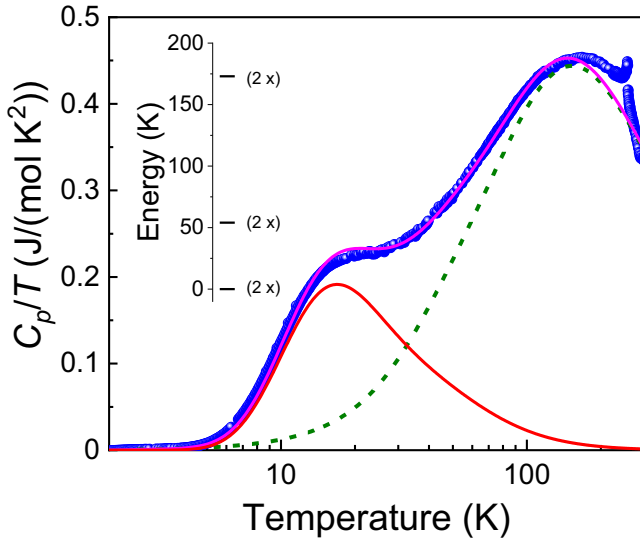


FIG. 14. (Blue dots) Specific heat capacity of CeCrO_3 divided by the temperature. The solid magenta line is a fit of the data below 225 K using a model combining contributions from the lattice heat capacity and magnetic heat capacity from Ce CEF excitations according to Eq. (5). The solid red line displays the heat capacity attributed to Ce and the green dashed line represents the heat capacity of the lattice. The inset outlines the energy sequence of Ce^{3+} crystal-field levels all double degenerate.

wherein the summation is carried out over all six crystal-field levels at energies E_i and p_i are the Boltzmann factors $p_i = \exp[-E_i/(k_B T)]$. Using Eq. (5) to fit the heat capacity data resulted in $T_{D1} = 257(3)$ K [$w_1 = 0.158(6)$], $T_{D2} = 634(20)$ K [$w_1 = 0.842(6)$], with $\sum_i w_i = 1$ and CEF energy levels shown in the inset to Fig. 14. The energies of the Ce^{3+} crystal-field levels were fitted to 0 K (doublet), to 54(2) K (doublet), and a doublet at $\sim 173(20)$ K, the latter level energy comes with a rather large error bar since its contribution to the magnetic heat capacity at higher temperatures is very small. The first two crystal-field levels which determine the essential contribution to the magnetic heat capacity appear to remain doubly degenerate, although a small splitting (~ 5 K) of the first excited doublet cannot be fully excluded. Overall, these findings point to small internal exchange field imposed by Cr on the Ce moments.

The CEF level sequence derived from the heat capacity gains support by an estimate of the temperature dependence of the magnetization. Particularly prominent in the magnetization of CeCrO_3 is the compensation of Cr and Ce magnetism leading to a transition to negative magnetizations below about 120 K (see, e.g., Fig. 3 in Ref. [29]) and a minimum at ~ 50 K. Figure 15 displays the magnetization determined by Cao *et al.* on a polycrystalline sample of CeCrO_3 in an external field of 1 kOe together with a calculation according to Eq. (8) for the Ce^{3+} magnetization assuming that the Ce moments are oppositely aligned to weak FM moment on the Cr atoms:

$$M_{\text{Ce}}(T) \propto \sum_n \mu_n \exp(-E_n/k_B T) / \sum_n \exp(-E_n/k_B T), \quad (8)$$

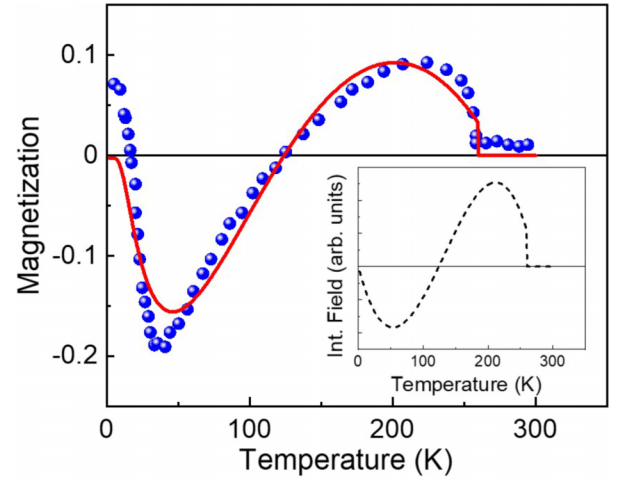


FIG. 15. (Blue dots) Magnetization determined on a CeCrO_3 polycrystalline sample in an external field of 1 kOe reported by Cao *et al.* [29]. The solid red line is a calculation of the magnetization according to Eq. (8) using the Ce^{3+} CEF levels obtained from the fit of the heat capacity. The Ce magnetization was assumed to be oppositely aligned to the magnetization of the Cr atoms.

where we have set $\mu_n = \pm \frac{1}{2} g_n$ and $E_n = \mu_n \mu_0 H_{\text{int}}$ and fitted an internal magnetic field, H_{int} imposed by the Cr moments (see inset to Fig. 15). Especially the minimum in the magnetization at ≈ 50 K is well reproduced assuming an energy separation of a first excited CEF doublet at 45 K, consistent with the energy of the first excited doublet fitted from the heat capacity data. The compensation point of the magnetization is found at ~ 125 K, consistent with the magnetization data. Interestingly, the g factor of the CEF ground-state doublet turns out to be very small, supporting the small Ce moment at low temperatures found by the NPD data.

D. Discussion and conclusions

Among the rare-earth orthochromites comprising a magnetic rare-earth cation, CeCrO_3 exhibits the highest Néel temperature of 260 K where antiferromagnetic order of the Cr sublattice takes place. Magnetization data indicated a weak ferromagnetic moment and an intricate magnetization compensation at about 120 K. CeCrO_3 crystallizes with the GdFeO_3 -type crystal structure with almost identical lattice parameters a and c . By using high-resolution neutron powder diffraction data, we have redetermined the Cr sublattice magnetic structure of CeCrO_3 . At 1.6 K, the Cr moments in CeCrO_3 order with a Γ_2 (C_x, G_y, F_z) magnetic configuration. Apart from a faint canting, the moments are essentially aligned along the crystallographic b axis (space group $Pnma$). The saturated magnitude of the Cr magnetic moments amounts to $\sim 2.54 \mu_B$. By using high-intensity medium-resolution neutron powder diffraction data, we found evidence for a faint canting of the Cr moments and very small C_x -type magnetic moments on the Ce^{3+} cations. Conclusive evidence for a weak ferromagnetic moment on the Cr atoms could not be derived from our neutron powder diffraction data.

Shukla *et al.* have proposed a magnetic structure solution for CeCrO_3 based on a prominent extra reflection at $d =$

4.47 Å and extra intensity at $d = 2.33$ Å which they ascribed to magnetic scattering of the Cr moments ($2.65 \mu_B$) [28]. Below 100 K an additional Bragg reflection at $d = 2.33$ Å was associated to ordering of the Ce moment for which they refined a saturated moment of $0.7 \mu_B$ at 22 K. Their G -type antiferromagnetic structure solution aligns the Cr moments of magnitude along the shorter axis in the a - b plane (a direction in $Pnma$ setting corresponding to the Γ_1 configuration) whereas the Ce moment is seen to adopt a C -type antiferromagnetic coupling along the same direction. Our findings cannot confirm their results, neither the moment direction of the Cr moment nor the size of the Ce moment.

While preparing this paper, Yadav *et al.* published the results of their neutron powder diffraction investigation on CeCrO_3 nanoparticles [32]. Combining their magnetization and neutron diffraction results Yadav *et al.* proposed a high-to low-temperature transition of the magnetic structure from Γ_4 to Γ_2 . However, due to the small difference between the pseudocubic lattice parameters they concluded that it was not possible to distinguish between three possible magnetic structures (Γ_1 , Γ_2 , Γ_4) based on their NPD data. Our results show now the Cr ordered magnetic moments to align at 1.6 K along the long b axis adopting a G -type antiferromagnetic arrangement according to Γ_2 supporting directly the conjecture of Yadav *et al.* concerning the existence of a spin reorientation. A direct proof for the existence of a spin reorientation from Γ_4 to Γ_2 must, however, await a confirmation of the supposed Γ_4 spin structure at high temperatures. Our own recent neutron diffraction experiments at high temperatures did not allow to make a conclusive statement as to the spin structure adopted below T_{N1} as the lattice parameters become even more pseudocubic at high temperatures [49].

We have analyzed new specific heat capacity data gained on a crystalline piece of CeCrO_3 to determine the crystal-electric-field splitting of the $^2F_{5/2}$ Hund's rule ground state of the Ce^{3+} cations. The results are used as input for a model calculation of the magnetization of CeCrO_3 which supports the Cr spin reorientation scenario and indicates that the complex temperature dependence of the magnetization of CeCrO_3 results from a compensation of the weak ferromagnetic component on the Cr atoms balanced by the Ce moments polarized by the internal exchange fields imposed by the Cr moments. This finding backs the assumption of spin reorientation starting from a Γ_4 -type Cr spin configuration at high temperatures to a Γ_2 configuration at low temperatures, as has also been observed for some other RCrO_3 systems [18]. Furthermore, we have determined in detail the magnetoelastic effects induced by the Cr moment antiferromagnetic ordering.

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DATA AVAILABILITY

The data that support the findings of this article are not publicly available upon publication because it is not technically feasible and/or the cost of preparing, depositing, and hosting the data would be prohibitive within the terms of this research project. The data are available from the authors upon reasonable request.

- [1] H. B. Lal, R. D. Dwivedi, and G. Gaur, Pyroelectric and dielectric properties of some heavy rare-earth orthochromites, *J. Mater. Sci.: Mater. Electron.* **7**, 35 (1996).
- [2] J. R. Sahu, C. R. Serrao, N. Ray, U. V. Waghmare, and C. N. R. Rao, Rare earth chromites: A new family of multiferroics, *J. Mater. Chem.* **17**, 42 (2007).
- [3] B. Rajeswaran, D. I. Khomskii, A. K. Zvezdin, C. N. R. Rao, and A. Sundaresan, Field-induced polar order at the Néel temperature of chromium in rare-earth orthochromites: Interplay of rare-earth and Cr magnetism, *Phys. Rev. B* **86**, 214409 (2012).
- [4] K. R. S. P. Meher, C. Martin, V. Caignaert, F. Damay, and A. Maignan, Multiferroics and magnetoelectrics: A comparison between some chromites and cobaltites, *Chem. Mater.* **26**, 830 (2014).
- [5] J. Prado-Gonjal, R. Schmidt, J.-J. Romero, D. Ávila, U. Amador, and E. Morán, Microwave-assisted synthesis, microstructure, and physical properties of rare-earth chromites, *Inorg. Chem.* **52**, 313 (2013).
- [6] M. Taheri, R. K. Kremer, S. Trudel, and F. S. Razavi, Exchange bias effect and glassy-like behavior of EuCrO_3 and CeCrO_3 nano-powders, *J. Appl. Phys.* **118**, 124306 (2015).
- [7] M. Taheri, F. S. Razavi, Z. Yamani, R. Flacau, P. G. Reuvekamp, A. Schulz, and R. K. Kremer, Magnetic structure, magnetoelastic coupling, and thermal properties of EuCrO_3 nanopowders, *Phys. Rev. B* **93**, 104414 (2016).
- [8] H. B. Lal, K. Gaur, R. D. Dwivedi, and N. Srivastava, Pyroelectric and dielectric properties of europium orthochromite, *J. Mater. Sci. Lett.* **8**, 1434 (1989).
- [9] C. N. R. Rao, A. Sundaresan, and R. Saha, Multiferroic and magnetoelectric oxides: The emerging scenario, *J. Phys. Chem. Lett.* **3**, 2237 (2012).
- [10] L. H. Yin, J. Yang, P. Tong, X. Luo, C. B. Park, K. W. Shin, W. H. Song, J. M. Dai, K. H. Kim, X. B. Zhu, and Y. P. Sun, Role of rare earth ions in the magnetic, magnetocaloric and magnetoelectric properties of RCrO_3 ($R = \text{Dy}, \text{Nd}, \text{Tb}, \text{Er}$) crystals, *J. Mater. Chem. C* **4**, 11198 (2016).
- [11] A. A. A. Qahtan, N. Zarrin, M. Fatema, H. A. S. Al-Shamiri, W. Khan, and S. Husain, A brief review on rare-earth chromites: Synthesis, properties and applications, *Phys. Scr.* **99**, 072001 (2024).
- [12] B. Pan, J. Fang, Q. Wu, N. Yu, M. Pan, Y. Yu, X. Hu, H. Ge, J. He, M. Zou, and H. Yang, Magnetic critical behavior and giant magnetocaloric effect in co-doping multiphase $\text{Gd}_{1-x}\text{Dy}_x\text{CrO}_3$ composites, *J. Alloys Compd.* **979**, 173586 (2024).
- [13] W. Koehler and E. Wollan, Neutron-diffraction study of the magnetic properties of perovskite-like compounds LaBO_3 , *J. Phys. Chem. Solids* **2**, 100 (1957).

- [14] E. Bertaut, *Spin Configurations of Ionic Structure: Theory and Practice*, in Magnetism, edited by G. T. Rado and H. Suhl, Vol. III (Academic, New York, 1963).
- [15] E. Bertaut, J. Mareschal, G. De Vries, R. Aleonard, R. Pauthenet, J. Rebouillat, and V. Zarubicka, A study of magnetostatic properties and magnetic structures of chromites of rare earth and yttrium, *IEEE Trans. Magn.* **2**, 453 (1966).
- [16] E. Bertaut and J. Mareschal, Etude de la structure magnetique des chromites d'erbium et de neodyme par diffraction neutronique, *Solid State Commun.* **5**, 93 (1967).
- [17] E. Bertaut, J. Mareschal, and G. De Vries, Etude par diffraction neutronique de la structure magnetique du chromite de terbium, *J. Phys. Chem. Solids* **28**, 2143 (1967).
- [18] R. Hornreich, Magnetic interactions and weak ferromagnetism in the rare-earth orthochromites, *J. Magn. Magn. Mater.* **7**, 280 (1978).
- [19] For convenience we provide a synopsis of how the irreducible representations Γ_i are related in the two mostly used settings of space group No. 62, $Pbnm$ and $Pnma$: $\Gamma_1 Pnma (G_x, C_y, A_z) \equiv \Gamma_1 Pbnm (A_x, G_y, C_z)$; $\Gamma_2 Pnma (C_x, G_y, F_z) \equiv \Gamma_2 Pbnm (F_x, C_y, G_z)$; $\Gamma_3 Pnma (F_x, A_y, C_z) \equiv \Gamma_3 Pbnm (C_x, F_y, A_z)$; $\Gamma_4 Pnma (A_x, F_y, G_z) \equiv \Gamma_4 Pbnm (G_x, A_y, F_z)$.
- [20] T. Sau, P. Yadav, S. Sharma, R. Raghunathan, P. Manuel, V. Petricek, U. P. Deshpande, and N. P. Lalla, High-resolution time of flight neutron diffraction and magnetization studies of spin reorientation and polar transitions in SmCrO_3 , *Phys. Rev. B* **103**, 144418 (2021).
- [21] N. Yuan, E. Walendy, N. Maraytta, W. Hergett, L. Bischof, M. Merz, and R. Klingeler, Anisotropic magnetic phase diagrams, tricriticality, and spin reorientation in high-pressure grown SmCrO_3 single crystals, *Phys. Rev. B* **111**, 174437 (2025).
- [22] P. Manuel, D. Khalyavin, F. Orlandi, L. Chapon, W. Xueyun, T.-H. Jang, E. S. Choi, and S.-W. Cheong, Magnetic structure determination of multiple phases in the multiferroic candidate GdCrO_3 , *Acta Crystallogr. Sect. B* **81**, 293 (2025).
- [23] A. H. Cooke, D. M. Martin, and M. R. Wells, Magnetic interactions in gadolinium orthochromite, GdCrO_3 , *J. Phys. C: Solid State Phys.* **7**, 3133 (1974).
- [24] L. Holmes, M. Eibschütz, and L. G. Van Uitert, Field-Induced spin reorientation in ErCrO_3 , *J. Appl. Phys.* **41**, 1184 (1970).
- [25] I. Fita, R. Puzniak, A. Wisniewski, and V. Markovich, Spin switching and unusual exchange bias in the single-crystalline GdCrO_3 compensated ferrimagnet, *Phys. Rev. B* **100**, 144426 (2019).
- [26] I. Fita, R. Puzniak, and A. Wisniewski, Pressure-tuned spin switching in compensated GdCrO_3 ferrimagnet, *Phys. Rev. B* **103**, 054423 (2021).
- [27] P. Jain, S. Sharma, R. Baumbach, A. K. Yogi, I. Ishant, M. Majumder, T. Siegrist, M. K. Chattopadhyay, and N. P. Lalla, Structural role in temperature-induced magnetization reversal revealed in distorted perovskite $\text{Gd}_{1-x}\text{Y}_x\text{O}_3$, *Phys. Rev. B* **109**, 094410 (2024).
- [28] R. Shukla, A. K. Bera, S. M. Yusuf, S. K. Deshpande, A. K. Tyagi, W. Hermes, M. Eul, and R. Pöttgen, Multifunctional nanocrystalline CeCrO_3 : Antiferromagnetic, relaxor, and optical properties, *J. Phys. Chem. C* **113**, 12663 (2009).
- [29] Y. Cao, S. Cao, W. Ren, Z. Feng, S. Yuan, B. Kang, B. Lu, and J. Zhang, Magnetization switching of rare earth orthochromite CeCrO_3 , *Appl. Phys. Lett.* **104**, 232405 (2014).
- [30] M. Taheri, F. S. Razavi, Z. Yamani, R. Flacau, C. Ritter, S. Bette, and R. K. Kremer, Structural, magnetic, and thermal properties of $\text{Ce}_{1-x}\text{Eu}_x\text{CrO}_3$ orthochromite solid solutions, *Phys. Rev. B* **99**, 054411 (2019).
- [31] In the older literature the setting $Pbnm$ for space group No. 62 has often been adopted. In our analysis we have consistently used the recommended (according to the International Tables) $Pnma$ setting of space group No. 62. The transformation from $Pbnm$ to $Pnma$ is $Pbnm:(c,a,b) \rightarrow Pnma:(a,b,c)$. For clarification, in the RCrO_3 phases the long crystal axis (7.7 Å) is the c axis in $Pbnm$ and the b axis in $Pnma$ setting.
- [32] M. Yadav, L. S. Kumar, K. Kumar, D. Das, Q. Zhang, and C. Rath, Evidence of spin reorientation from Γ_4 to Γ_2 and sign reversal exchange bias in CeCrO_3 nanoparticles, *Phys. Status Solidi B* **262**, 2400372 (2025).
- [33] M. Taheri, The structural, magnetic and thermal studies of $\text{Ce}_{1-x}\text{Eu}_x\text{CrO}_3$ nano-powders, Ph.D. thesis, Brock University, 2015.
- [34] For typical characteristics of ILL's high-resolution two-axis diffractometer D2B see <https://www.ill.eu/users/instruments/instruments-list/d2b/characteristics>.
- [35] Th. C. Hansen, P. F. Henry, H. E. Fischer, J. Torregrossa, and P. Convert, The D20 instrument at the ILL: a versatile high-intensity two-axis neutron diffractometer, *Meas. Sci. Technol.* **19**, 034001 (2008).
- [36] J. Rodríguez-Carvajal, Recent advances in magnetic structure determination by neutron powder diffraction, *Phys. B (Amsterdam)* **192**, 55 (1993).
- [37] See Supplemental Material at <http://link.aps.org/supplemental/10.1103/mgs3-xj3v> for the temperature dependence of the lattice parameters and the atom positional parameters.
- [38] K. Oikawa, T. Kamiyama, T. Hashimoto, Y. Shimojo, and Y. Morii, Structural phase transition of orthorhombic LaCrO_3 studied by neutron powder diffraction, *J. Solid State Chem.* **154**, 524 (2000).
- [39] M. Abramowitz and I. A. Stegun, *Handbook of Mathematical Functions with Formulas, Graphs and Mathematical Tables*, National Bureau of Standards Applied Mathematics Series, Vol. 55 (U.S. GPO, Washington, DC, 1972), p. 998.
- [40] E. Scheer, J. Wosnitza, H. Löhneysen, R. Kürsch, M. Lang, and F. Steglich, Critical exponents of eute from specific-heat and thermal-expansion measurements, *J. Magn. Magn. Mater.* **104–107**, 175 (1992).
- [41] C. Ritter, M. Ceretti, and W. Paulus, Determination of the magnetic structures in orthoferrite CeFeO_3 by neutron powder diffraction: First order spin reorientation and appearance of an ordered Ce-moment, *J. Phys.: Condens. Matter* **33**, 215802 (2021).
- [42] A. Patterson, The Scherrer formula for x-ray particle size determination, *Phys. Rev.* **56**, 978 (1939).
- [43] R. Kubo, The spin-wave theory of antiferromagnetics, *Phys. Rev.* **87**, 568 (1952).
- [44] T. Oguchi, Theory of spin-wave interactions in ferro- and antiferromagnetism, *Phys. Rev.* **117**, 117 (1960).
- [45] P. W. Anderson, An approximate quantum theory of the antiferromagnetic ground state, *Phys. Rev.* **86**, 694 (1952).
- [46] Y. Zhu, J. Xia, S. Wu, K. Sun, Y. Yang, Y. Zhao, H. W. Kan, Y. Zhang, L. Wang, H. Wang, J. Fang, C. Wang, T. Wu, Y. Shi, J. Yu, R. Zhang, and H.-F. Li, Crystal growth engineering and

- origin of the weak ferromagnetism in antiferromagnetic matrix of orthochromates from t-e orbital hybridization, [Science](#) **25**, 104111 (2022).
- [47] J. H. Van Vleck, On the theory of antiferromagnetism, [J. Chem. Phys.](#) **9**, 85 (1941).
- [48] R. J. Goetsch, V. K. Anand, A. Pandey, and D. C. Johnston, Structural, thermal, magnetic, and electronic transport properties of the $\text{LaNi}_2(\text{Ge}_{1-x}\text{P}_x)_2$ system, [Phys. Rev. B](#) **85**, 054517 (2012).
- [49] C. Ritter, R. K. Kremer, and F. S. Razavi (unpublished).