Impact of Rare-earth site Substitution on the Structural, Magnetic and Thermal Properties of Ce$_{1-x}$Eu$_x$CrO$_3$ Orthochromite Solid-solutions

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The role of slight changes of the chemical composition on antiferromagnetic ordering of Cr in rare-earth orthochromites was investigated on a series of ceramic solid-solutions Ce$_{1-x}$Eu$_x$O$_3$ where x varied from 0 to 1. Gradual replacement of Ce by Eu reduces the cell volume and acts equivalently to applying external pressure. Full replacement of Ce by Eu, on the other hand, reduces the Néel temperature from 260 K for CeCrO$_3$ to 178 K for EuCrO$_3$ as established by magnetization, heat capacity and neutron powder diffraction measurements. High resolution x-ray powder diffraction measurements on Ce$_{1-x}$Eu$_x$O$_3$ and neutron powder diffraction studies on CeCrO$_3$ enable to correlate the magnetic properties of the Cr magnetic subsystem with the size of the lattice and minute changes of the bonding and torsion angles within and between the CrO$_6$ octahedra. We find that the sizes and the shapes of the CrO$_6$ octahedra remain essentially unchanged as the size of the rare-earth cations is reduced whereas decreasing Cr - O - Cr bonding angles and increasing inclination of neighboring octahedra enable to compensate for the decreasing lattice size.

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I. INTRODUCTION

Rare-earth orthochromites which crystallize with the orthorhombic GdFeO$_3$ structure-type (Figure 1) have attracted special attention, because they may exhibit ferroelectric polarization either induced by an external magnetic field or spontaneous polarization due to internal magnetic fields induced by long-range magnetic ordering. For example, magneto-electric effects as well as magnetic and electric field induced switching of the dielectric polarization have been detected in SmCrO$_3$, GdCrO$_3$, and ErCrO$_3$. Still controversial is the relevance of the interaction between the rare-earth magnetism and the weak ferromagnetism due to spin canting in the Cr subsystem. For example, polarization in ErCrO$_3$ vanishes at a spin re-orientation transition at $\sim 22$ K below which spin canting of the Cr moments also disappears emphasizing the importance of weak ferromagnetism and the interaction with the rare-earth subsystem for polar ordering. For LuCrO$_3$, on the other hand, Preethi Meher et al. observed qualitatively similar ferroelectric-like characteristics as in ErCrO$_3$, though weaker in magnitude, revealing that orthochromites with a diamagnetic rare-earth constituent can also develop a polar state questioning the necessity of rare-earth magnetism for establishing multiferroicity in the orthochromites. At present, there are also diverging conclusions as to whether the multiferroic state as evidenced by polarization and pyroelectric currents occurs below the Néel temperature or whether it is already formed at higher temperatures. Ghosh et al. have observed that in SmCrO$_3$ and HoCrO$_3$ polar order already develops in the paramagnetic state and they attributed this observation to a structural transition from the centrosymmetric orthorhombic space group $Pbnm$ to the non-centrosymmetric space group $Pna2_1$. Kumar et al. recently suggested that an additional driving force for observation of ferroelectricity in rare-earth orthochromites is the short range exchange interactions.

The range of the magnetic ordering temperatures of the RCrO$_3$ opens up potential applications for these compounds. Compared to what has been observed, for example, in the orthomanganites family, RMnO$_3$, (e.g. $T_N \sim 27$ K in TbMnO$_3$) which comprises some of the most prominent multiferroic systems, the rare-earth orthochromites exhibit ordering temperatures close to room temperature. Also, since the coupling between the $4f$ and the $3d$ electrons in the half filled $t_{2g}$ orbitals of the Cr$^{3+}$ cations can be large, orthochromites may have some advantages compared to orthoferrites. Although the latter exhibit higher magnetic ordering temperatures, Cr$^{3+}$ lacks fourth order crystal field splitting terms acting on the $S=\frac{3}{2}$ spin multiplet (cf. Ref. 15). This might allow higher complexity of spin canting and spin reorientation phenomena in the magnetic structures of the rare-earth orthochromites.

The structural and magnetic properties of the rare-
earth orthochromites, RCrO$_3$, have been studied in some
detail before.\cite{1,2,3,4} By using high-resolution neutron
powder diffraction, Zhou \textit{et al.} determined the crystal
structures including the oxygen atom positions with great
precision.\cite{12} They found that the cooperative rotation and
tilting of the CrO$_6$ octahedra essentially tunes the $t_{2g}$ - $e_g$
overlap and the Cr - O - Cr superexchange which can ex-
plain the sizeable decrease of the Néel temperature when
substituting smaller rare-earth cations. The Néel tem-
perature, $T_N$, of the Cr substructure is at about
300 K for LaCrO$_3$ decreases monotonically as the rare-
earth element is replaced by a heavier one with $T_N$ for
LuCrO$_3$ of about 100 K.\cite{13} CeCrO$_3$, studied by Shukla \textit{et al.}, exhibits a Néel temperature of ~260 K close to that
of LaCrO$_3$\cite{13} EuCrO$_3$ orders at ~178 K with a slightly
canted antiferromagnetic structure.\cite{10}

\begin{figure}[h]
  \centering
  \includegraphics[width=\textwidth]{fig1.png}
  \caption{(color online) Crystal structure of (Ce,Eu)CrO$_3$
in space group \textit{Pnma} (no. 62). Yellow/green and blue
spheres represent cerium/europium and chromium atoms,
respectively. The O2 atoms connecting the CrO$_6$ octahedra in
the $a$ - $c$ plane are given by red spheres and the O1 atoms
connecting along $b$ are represented by magenta spheres. A
unit cell is outlined.}
\end{figure}

The marked decrease of the Néel temperature of the
Cr substructure in the series from the light to the heavy
rare-earth elements with the simultaneous reduction of
the unit cell volume already were suggestive that the Cr
- Cr distances alone cannot be the determining factor
for the Cr magnetic ordering in the RCrO$_3$. Rather,
as concluded by Zhou \textit{et al.} bonding and tilting an-
gles of the CrO$_6$ octahedra change and the crystal structure
becomes more distorted, reducing Cr - O - Cr elec-
tron transfer and in turn superexchange between the Cr
cations.\cite{12} Bhadram \textit{et al.} have investigated the variation
of the room temperature lattice parameters and Ram-
man frequencies of RCrO$_3$ (R = Eu, Gd, Tb, Lu) with
pressure and found that the octahedral tilts decrease lin-
early with increasing R radii.\cite{15} Compressibility increases for small R ions whereas the structures of rare-earth or-
thochromites with larger R ions are stiffer. They con-
cluded that for the Néel temperature the Cr - O bond
lengths play a dominant role over the octahedral tilts.\cite{17}
Zhao \textit{et al.} using first-principles calculations found oppo-
site dependence of the Néel temperature on hydrostatic
or chemical pressure.\cite{15} Whereas, hydrostatic pressure in-
creases the Néel temperature chemical pressure e.g. in-
duced by replacing larger rare-earth cations by smaller
ones lowers the Néel temperature, in qualitative agree-
ment with the Néel temperatures observed across the se-
ries of the rare-earth orthochromites.

For CeCrO$_3$ ($T_N$ ~260 K) Shukla \textit{et al.} found a G-
type magnetic ordering of the Cr substructure and also
proposed ordering of the Ce moments below ~100 K and
a spin re-orientation below ~15 K. However, this conclu-
sion was based on very faint additional magnetic scat-
tering peak in the neutron powder diffraction patterns
at temperatures well below ~100 K.\cite{15} The refined Ce
moments amounted to ~0.7 $\mu_B$ and pointed antiparal-
lel to the Cr moments. In preceding publications, we
have investigated in detail the magnetic properties of
EuCrO$_3$ and CeCrO$_3$.\cite{16,17} Below 178 K, the Cr substruc-
ture in EuCrO$_3$ orders with a G$_2$-type antiferromagnetic
structure with an ordered moment of ~2.4 $\mu_B$, consist-
tent with the $S = \frac{3}{2}$ spin-only ground state. A weak
canted ferromagnetic moment pointing along the c-axis
($Pbnm$ notation) could be concluded from the neutron
diffraction investigation. It amounts to ~0.1 $\mu_B$, consist-
tent with single crystal magnetization data.\cite{22} Evidence
for ordering of the Eu moments has neither been found
in the neutron powder diffraction data nor in the heat
capacity or magnetization data. This observation can
be understood as being due to the $J = 0$ Hund’s rule
ground state and the van Vleck-type temperature depen-
dent moment of the Eu$^{3+}$ cations.\cite{16} In contrast to the
absence of conclusive evidence for R moment ordering in
CeCrO$_3$ and EuCrO$_3$, there is some unusual behavior of
the magnetic susceptibilities at low temperature.\cite{15,16} Es-
pecially, the field-cooled (FC) susceptibility of CeCrO$_3$
showed a compensation point at ~50 K with negative
magnetization below. Irrespective of the measuring field,
zero-field cooled (ZFC) and FC magnetic susceptibilities
intersected at ~100 K with the FC susceptibility being
smaller than the ZFC susceptibility. This complex be-
havior could be due to inhomogeneity in the small sample
grains (typically < 100 nm, “core-shell” behavior) or be
due to some complex compensation of R and Cr moments
induced by external fields.\cite{23}

We explore in this paper the changes of the magnetic
and structural properties induced by the replacement of
a larger rare-earth cation Ce$^{3+}$ by the smaller one Eu$^{3+}$
with ionic radii of 1.283 Å and 1.144 Å, respectively.\cite{21}
Especially, we study in detail the changes of the crystal
structure and magnetic properties in small steps with a
series of solid-solutions of CeCrO$_3$ and EuCrO$_3$, the lat-
ter having unit cell volumes of 230.8 Å$^3$ and 224.8 Å$^3$,
respectively. Gradual replacement of Ce with Eu leads to
an increase of the cell distortion factor\cite{15} by ~ 50%
similar to the effect of external hydrostatic pressure of ~10 GPa or more. On the other hand, EuCrO$_3$ has a markedly lower Neél temperature than CeCrO$_3$ suggesting that substituting Ce by the smaller Eu cations i.e. chemical pressure will act differently from hydrostatic pressure, supporting the first-principles results obtained by Zhao et al.\cite{zhao2013}

The paper is organized in two parts, followed by a summary: We first describe structural properties of the Ce$_{1-x}$Eu$_x$CrO$_3$ phases across the entire solid-solution range $0 \leq x \leq 1$. This set of solution-solids allows to tune the mean ionic radius of the rare-earth cations between those of Ce and Eu, thus covering continuously a range which was accessed by high-resolution neutron powder diffraction for NdCrO$_3$ and PrCrO$_3$ only. Samples containing Sm, Eu, and Gd orthochromites were not included in this series.\cite{weber2012}

In the second part, we present the results of our temperature, field and thermal history dependent of dc and ac magnetic susceptibilities and thermal properties and report first neutron powder diffraction investigations on the solid solutions Ce$_{1-x}$Eu$_x$CrO$_3$. Finally, we discuss the results and summarize.

II. EXPERIMENT

Powder samples of Ce$_{1-x}$Eu$_x$CrO$_3$ were synthesized by the solution combustion method starting from equimolar solutions of high purity cerium and europium nitrate, chromium nitrate and glycine as described in detail elsewhere.\cite{weber2012, morita2012}

The products were characterized with respect to phase purity by x-ray powder diffraction (XRPD) at room temperature using MoK$_{\alpha 1}$ radiation ($2\theta_{\text{max}} \sim 110^\circ$, STOE triple DECTRIS MultiMYTHEN silicon strip detector). Neutron powder diffraction (NPD) patterns of CeCrO$_3$ were collected at room temperature on the high-resolution two-axis diffractometer D2B installed at the Institut Laue-Langevin (ILL, Grenoble) using neutrons of 1.594 Å wavelength. The polycrystalline sample of ~9 g was contained in a thin-walled vanadium container of 8 mm outer diameter. Rietveld refinements by varying lattice parameters and atom positions were performed in the orthorhombic spacegroup $Pnma$ (no. 62) using the FullProf or the TOPAS software\cite{martnez2015} assuming a Thompson-Cox-Hastings pseudo-Voigt peak profile (FullProf NPR = 7). Isotropic and anisotropic displacement parameters were tested in case of the x-ray and neutron diffraction patterns, respectively. Since marked anisotropies could not be seen we report isotropic displacement parameters in the following. The background was modeled by a higher-order Chebychev polynomial. The refinements typically converged to Bragg- and Rf-reliability factors of ~ 2% or less and $\chi^2$-values better than 1 were achieved for the x-ray patterns. For the neutron diffraction pattern of CeCrO$_3$, the reliability factors were somewhat larger (see Table I). Medium resolution high intensity neutron scattering was performed on the N5 triple axis spectrometer at the Chalk River Laboratories in order to follow the temperature dependence of magnetic Bragg peaks. Initial and final neutron energies were chosen by the pyrolytic graphite PG002 reflections. In order to reduce the high absorption cross section for thermal neutrons from the $^{151}$Eu isotope in the natural isotope composition of Eu, the samples with a Eu content larger than 10% were contained in flat geometry thin-walled aluminum sample holders which were long enough to cover the full beam height, but reduced the thickness of the sample to ~1 mm.\cite{weber2012} dc magnetization were measured using a Magnetic Property Measurement System (Quantum Design, MPMS). Heat capacity measurements were performed on compressed pellets in a Physical Property Measurement System (Quantum Design, PPMS). The particle size of the powders was determined with a Hitachi H-7650 transmission electron microscopy (TEM) and a Zeiss Sigma VP scanning electron microscopy (SEM) equipped with the Oxford Inca EDX.

III. RESULTS

A. Chemical and Structural Characterization

Chemical and structural properties and the morphology of the boundary phases CeCrO$_3$ and EuCrO$_3$ as well as a surface analysis of the Ce$_{1-x}$Eu$_x$CrO$_3$ nano-powders have been described in detail elsewhere.\cite{weber2012, morita2012, weber2013, weber2014, weber2015} Figure 2 summarizes typical result of our EDX microprobe analysis and the TEM picture of the sample Ce$_{0.9}$Eu$_{0.1}$CrO$_3$. A statistical analysis of the sample grain sizes indicated a Gaussian distribution with a maximum at ~75 nm and a FWHM of ~50 nm, similar to what has been reported for pure CeCrO$_3$ and EuCrO$_3$.\cite{weber2012, morita2012, weber2013, weber2014, weber2015}

![FIG. 2. (color online) (a) EDX diagram of the phase Ce$_{0.9}$Eu$_{0.1}$CrO$_3$. (b) TEM image with corresponding size distribution histogram (inset) of the same sample. The red solid line is a Gaussian centered at ~75 nm and a FWHM of ~50 nm.](image)

The results of our NPD on CeCrO$_3$ and the XRPD experiments on Ce$_{1-x}$Eu$_x$CrO$_3$ together with the Rietveld refinements are shown in Figures 3 and 4a - c). The comparison of the refined structural parameters compiled in Table I reveals good agreement between parameters refined from our XRPD and NPD patterns and previously reported data.\cite{weber2012, morita2012, weber2013, weber2014, weber2015} Merely some atom positional parameters of the two oxygen atoms O1 (Wyckoff site 4c) and

![FIG. 3. (color online) Plots of the crystallographic cell parameters a, b, c and α, β, γ vs. Eu content x for Ce$_{1-x}$Eu$_x$CrO$_3$ and CeCrO$_3$.](image)
TABLE I. Structural parameters and conventional reliability factors as obtained from Rietveld profile refinements of our XRPD and NPD patterns collected at 295 K with Mo-K\(_{\alpha1}\) radiation and neutrons with a wavelength of \(\lambda = 1.549\) Å on CeCrO\(_3\). The Rietveld refinements were performed assuming the space group \(Pnma\) (no. 62). The respective site occupancies were not refined from the XRPD pattern whereas the refinement of the NPD pattern indicated full occupation as of the oxygen sites. Data by Shukla et al.\(^{15}\) are given in the rightmost column.

| T (K)     | 295 (XRPD) | 295 K (NPD) | 300 K (NPD) |
|-----------|------------|-------------|-------------|
| a (Å)     | 5.4736(1)  | 5.4729(2)   | 5.472(1)    |
| b (Å)     | 7.7311(1)  | 7.7304(3)   | 7.733(1)    |
| c (Å)     | 5.4818(1)  | 5.4808(2)   | 5.479(1)    |
| V (Å\(^3\)) | 231.97(1)  | 231.88(2)   | 231.84(11)  |
| Ce (4c)   | x          | 0.5280(1)   | 0.5272(6)   | 0.5294(20)  |
|           | y          | 1/4         | 1/4         | 1/4         |
|           | z          | 0.5050(2)   | 0.5046(2)   | 0.5054(9)   |
|           | \(B_{iso}\) (Å\(^2\)) | 0.35(1)     | 0.32(1)     | 0.5         |
| Cr (4b)   | x          | 0           | 0           | 0           |
|           | y          | 0           | 0           | 0           |
|           | z          | 1/2         | 1/2         | 1/2         |
|           | \(B_{iso}\) (Å\(^2\)) | 0.24(1)     | 0.23(1)     | 0.5         |
| O1 (4c)   | x          | 0.9856(7)   | 0.9902(7)   | 0.9948(15)  |
|           | y          | 1/4         | 1/4         | 1/4         |
|           | z          | 0.4220(15)  | 0.4304(7)   | 0.4260(14)  |
|           | \(B_{iso}\) (Å\(^2\)) | 0.23(5)     | 0.24(1)     | 0.9         |
| O2 (8d)   | x          | 0.2831(9)   | 0.2834(4)   | 0.2821(7)   |
|           | y          | 0.0358(7)   | 0.0391(3)   | 0.0389(6)   |
|           | z          | 0.7192(9)   | 0.7146(5)   | 0.7201(8)   |
|           | \(B_{iso}\) (Å\(^2\)) | 0.23(5)     | 0.29(1)     | 0.9         |
| Bragg R-factor (%) | 1.54 | 3.94 | |
| \(R_I\)-factor (%) | 1.86 | 2.96 | |

TABLE II. Interatomic distances and bonding angles of CeCrO\(_3\) calculated from the parameters given in Table I. The angles \(\alpha\) and \(\beta\) are defined as the O21 - Cr - O22 bonding angle in the midsection of the CrO\(_6\) octahedra and the torsion angle \(\beta\) is given by the tilt of the Cr - O1 direction with respect to a neighboring Cr - O1 bonds.

|                | XRPD     | NPD      |
|----------------|----------|----------|
| Cr - O21 (Å)   | 1.964(5) | 1.969(3) |
| Cr - O22 (Å)   | 1.980(5) | 1.986(3) |
| Cr - O1 (Å)    | 1.981(2) | 1.9706(8) |
| \(\alpha\) (°) | 88.72(16) | 88.65 (11) |
| \(\beta\) (°)  | 89.61(5) | 89.25(4) |
| \(\angle\) O1 - Cr - Cr - O1 (°) | 15.61(4) | 16.7(4) |
| \(\angle\) Cr - O2 - Cr (°)  | 158.2(3) | 156.50(15) |

O2 (Wyckoff site 8d) differ slightly which also explains the small differences in the Cr - O - bonding angles. The angle \(\alpha\) which reflects the O21 - Cr - O22 bonding angle in the equatorial plane of the CrO\(_6\) octahedra and the angle \(\beta\) which measures the tilt of the Cr - O1 direction with respect to the plane spanned by the O2 atoms and the Cr atoms are very close to 90° and less different and agree well for both techniques and previously published data. The characteristic Cr - O distances and O - Cr - O bonding angles are compiled in Table II.

The high absorption cross section of the element Eu with the natural isotope composition usually prevents high-resolution NPD measurements on Eu substituted samples. In order to follow the variation of the crystal structure and especially the shifts of the oxygen atoms of Eu substituted samples, Ce\(_{1-x}\)Eu\(_x\)CrO\(_3\), we therefore used the lattice and positional parameters determined from the refinement of the XRPD patterns. The XRPD patterns of a total of nine phases of Ce\(_{1-x}\)Eu\(_x\)CrO\(_3\) (0 \(\leq\) x \(\leq\) 1) and that of GdCrO\(_3\) were measured and Rietveld refinements were performed. Fig. 3(a - c) displays three characteristic diffraction patterns covering the entire range of x compared with the results of the refinements and the difference between observed and calculated patterns. In addition to the lattice parameters and the atom positions shown in the following figures (cf. Fig. 5 - 8), background and displacement parameters have also been refined which will not be discussed any further.

Fig. 5 summarizes the lattice parameters and the cell volume of the phases Ce\(_{1-x}\)Eu\(_x\)CrO\(_3\) versus the Eu content. The cell volume decrease linearly with a magnitude which is in good agreement with previous findings. Whereas a and c follow a Vegard’s-law with a linear decrease.
FIG. 4. (color online) The XRPD patterns of Ce_{1-x}Eu_{x}CrO_3 (x = 0.0, 0.5, 1.0, from bottom to top) collected at room-temperature with λ = 0.709319 Å (Mo Kα). Black circles represent the measured data, the red solid line is the result of the Rietveld refinement. The blue solid line at the bottom of the graph shows the difference between the observed and calculated patterns. Vertical tics (blue) mark angles of the Bragg reflections used to simulate the refined patterns.

FIG. 5. (color online) (a) Cell volume and lattice parameters a, b and c versus the Eu content x for the phases Ce_{1-x}Eu_{x}CrO_3 (Pnma setting). The inset shows the crossing of the lattice parameters a and c for small x. The colored dashed lines are guides to the eye. The black dashed line in (c) emphasizes the non-Vegard’s behavior of the lattice parameter c.

d = 10^6 \times (a/\sqrt{2} - a_p)^2 + (b/2 - a_p)^2 + (c/\sqrt{2} - a_p)^2)/a_p^2/3, \quad (1)

where the average ‘cubic’ lattice parameter a_p is given by

a_p = (a/\sqrt{2} + b/2 + c/\sqrt{2})/3. \quad (2)

d shows a maximum distortion of ~ 150 ppm for EuCrO_3 (cf. Fig. 6), whereas for CeCrO_3 d almost vanishes. Compared to the high pressure data by Venkata et al. a cell distortion factor of 150 ppm is comparable to distortion factors obtained for example in EuCrO_3.

The cell distortion factor, d, introduced by Sasaki et al. to measure the deviation of distorted perovskite-type structures from cubic symmetry is estimated according to \[d = 10^6 \times (a/\sqrt{2} - a_p)^2 + (b/2 - a_p)^2 + (c/\sqrt{2} - a_p)^2)/a_p^2/3,\]

where the average ‘cubic’ lattice parameter \(a_p\) is given by \[a_p = (a/\sqrt{2} + b/2 + c/\sqrt{2})/3.\]

\[d\] shows a maximum distortion of ~ 150 ppm for EuCrO_3 (cf. Fig. 6), whereas for CeCrO_3 \(d\) almost vanishes. Compared to the high pressure data by Venkata et al. a cell distortion factor of 150 ppm is comparable to distortion factors obtained for example in EuCrO_3.
for pressures of $\sim 10$ GPa. Remarkable is the negative slope of the distortion factor, for small, values of $x \leq 0.04$ below the intersection of the lattice parameters $a$ and $c$ (cf. inset Fig. 6) paralleling the crossing of the lattice parameters $a$ and $c$ in this concentration range.

The gradual replacement of the larger Ce$^{3+}$ cations by the smaller Eu$^{3+}$ cations leads to systematic shifts of the atoms in the crystal structures of the phases Ce$_{1-x}$Eu$_x$CrO$_3$ with about the same magnitude for all atoms involved (R, O1, and O2). Figure 7 summarizes our results for the R and the O1 positional parameters. The $z$ and $x$ coordinates of the Ce/Eu atoms are linearly related. Both are slightly decreasing with a growing Eu content. In the inset to Fig. 7(a), we highlight a projection of the crystal structure of Ce$_{0.8}$Eu$_{0.2}$CrO$_3$ along [010] with arrows representing the atom shifts resulting from a 80% replacement ($x = 0.8$) of Ce by Eu cations. The Ce/Eu atoms move in the $a$ - $c$ plane away from the symmetric (1/2,1/4,1/2) position with the movement along $<100>$ being somewhat more pronounced. In contrast to the R atoms, the tilting of the apical oxygen atoms O1 away from $<010>$ with an increasing Eu content is more complex: As revealed by a plot of the coordinate $z_{O1}$ versus $x_{O1}$ the movement of the O1 atoms splits into two separate branches with a significantly different dependence on $x$. For a small Eu content ($x < 0.04$) $z_{O1}$ is almost independent of $x_{O1}$, whereas for ($x > 0.04$) one observes a linear relationship of $z_{O1}$ versus $x_{O1}$ which reflects a correlated tilting of the CrO$_6$ octahedra into the $a$ - $c$ plane away from a stretched configuration.

The apical oxygen atoms O1 move only slightly away from a orthogonal orientation with respect to the Cr - O2 equatorial plane in the CrO$_6$ octahedra. Figure 8 shows a maximum “skewness” of less than 2$^\circ$ with an opposite movement of $\angle$ (O22 - Cr - O1) and $\angle$ (O21 - Cr - O1) around an average value of $\sim 90$ deg. This tilting of the CrO$_6$ octahedra leads to an increased torsion of neighboring CrO$_6$ octahedra with respect to each other (cf. Figure 9(b)). The torsion angle O1 - Cr - Cr - O1 exhibits a linear dependence on the Eu content and increases markedly by about 22%. The torsion angle is linearly correlated with the Cr - O2 - Cr bonding angle (cf. Figure 9(c)). The latter characterizes the opposite movement of the O2 equatorial oxygen atoms outward and inward away from a 180$^\circ$ Cr - O - Cr bond as displayed in Fig. 9(b).

Figure 10 summarizes the Cr - O distances in the CrO$_6$ octahedra. The Cr - O2 distances (Cr-O21 and Cr - O22, i.e. the distance to the O atoms which lie essentially in the $a$ - $c$ plane in $Pnma$ setting) exhibit an opposed $x$ dependence with about the same magnitude of the slopes. The Cr - O1 distance to the apical oxygen atoms essentially parallel $b$ undergoes a moderate elongation. An estimation of the octahedral distortion factor which we defined in analogy of the cell distortion factor according
FIG. 8. (color online) O2 - Cr - O1 angles derived from our neutron diffraction data (black circles and squares) and the x-ray diffraction (red circles and squares) measurements. Dashed lines are guides to the eye. Literature data are also plotted: (green) asterisks CeCrO$_3$ (brown) diamond GdCrO$_3$.

\[
d_{\text{oct}} = \frac{1}{6} \sum_{i=1}^{6} (d_{iCr-O} - d_{\text{ave}})^2, \quad (3)
\]

where the mean distance, $d_{\text{ave}}$, is calculated from the six Cr to oxygen distances in the CrO$_6$ octahedra, and $d_{iCr-O}$, using

\[
d_{\text{ave}} = \frac{1}{6} \sum_{i=1}^{6} d_{iCr-O}, \quad (4)
\]

indicates an octahedral distortion between 5 and 10 ppm (cf. Figure 10(d)), largely independent of the Eu content.

B. Magnetic Properties

The temperature dependence of the dc magnetizations in an applied magnetic field of $\mu_0H = 0.05$ T of several polycrystalline samples of Ce$_{1-x}$Eu$_x$CrO$_3$ was measured in a warming cycle after the samples had been slowly cooled ($\sim$1.5 K/min) either with zero field (ZFC) or magnetic field (FC). The ZFC and FC data summarized in Figure 11 reveal an antiferromagnetic ordering of the Cr moments. The Néel temperature decreases from 260 K (CeCrO$_3$) to 178 K (EuCrO$_3$). Small peaks are seen in the ZFC traces whereas the FC magnetizations exhibit a sharp increase reminiscent of the built-up of spontaneous magnetization in a ferro- or ferrimagnet. These anomalies become more pronounced with increasing Eu content $x$. In addition, the ZFC magnetizations show maxima below $\sim$ 70 K, especially for smaller Eu contents ($x < 0.5$) and negative magnetization which is attributed to the development of rare-earth magnetic ordering. The inset in Figure 11(a) shows, for example, the ZFC (blue solid line) and the FC (red solid line) susceptibilities of CeCrO$_3$ ($x = 0.0$) which bifurcate from each other at a splitting temperature of $\sim$258 K. By warming up from 1.8 K to room temperature, $\chi$(ZFC) decreases gradu-
ally until it reaches the transition temperature at $T_N \sim 260$ K in good agreement with previous studies on orthochromites. $\chi$(ZFC) is positive at all temperatures, whereas in FC measurements the susceptibility (red line) increases up to the transition temperature of $T_1 \sim 12$ K and then decreases again to become zero at the compensation temperature, $T_{\text{comp}}$. Below $T_{\text{comp}}$, the magnetization is negative while with further warming, it changes back to positive values. Above $T_{\text{comp}}$, the magnetization increases to attain a maximum at $T_b \sim 220$ K and then decreases gradually to reach the transition temperature $T_N \sim 260$ K. The $T_1$ anomaly may be ascribed to the magnetic ordering of cerium ions which similarly has been seen as the spin reorientation in different members of RCrO$_3$ compounds. Interestingly, Ce ordering appears to have no immediate impact on the Cr magnetic structure as the intensity of the (110)/(011) magnetic Bragg reflection follows an standard order parameter temperature dependence (see discussion and Figure 13 below).

![Graph](image)

**FIG. 10.** (color online) (a - c) (black) square Cr-to-oxygen interatomic distances derived from our neutron powder diffraction data and the x-ray diffraction (red) circles patterns. Dashed lines are guides to the eye. The upper left inset in (b) gives the assignment of the O21 and O22 atoms. Octahedral distortion factor according to Eq. (3). Literature data are also plotted: (blue) circles RCrO$_3$ ($R =$ Nd, Pr, Tb) (green) asterisk CeCrO$_3$ (brown) diamond GdCrO$_3$. (d) The octahedral distortion factor calculated from the distances in (a) - (c) according to Eq. (3). The dashed area indicates an interval of 3σ around an mean value of 7.5 ± 0.9.

**FIG. 11.** (online color) (a) ZFC and (b) FC susceptibilities versus temperature of polycrystalline samples of Ce$_{1-x}$Eu$_x$CrO$_3$ ($x=0.1, 0.5, 0.9$ and 0.95) under an applied magnetic field of 500 Oe. The inset in (a) shows the temperature dependence of ZFC and FC susceptibilities of CeCrO$_3$.

### C. Heat Capacities

The heat capacities of most rare-earth orthochromites, RCrO$_3$ ($R =$ La, Pr, Nd, Sm, Gd, Dy, Ho, Er and Y) have been reported by Satoh et al. [30] and Su et al. [37,39]. In this work, we measured the heat capacities on Ce$_{1-x}$Eu$_x$CrO$_3$ phases down to liquid helium temperature at zero magnetic field and studied the anomalies associated with the long-range magnetic ordering of Cr$^{3+}$ ions. Figure 12 displays the temperature dependence of the heat capacity of the Ce$_{1-x}$Eu$_x$CrO$_3$ from 1.8 K to 300 K in zero magnetic field where $x =$
The long-range ordering of the Cr$^{3+}$ moments indicated by the $\lambda$-shaped anomaly shifts from 256 K for $x = 0.0$ to 175 K for $x = 1.0$. Especially for small Eu contents, the heat capacities at low temperatures revealed additional magnetic contributions. These can be clearly separated from the total heat capacities when the heat capacities of the lattice were subtracted. The lattice heat capacities were estimated from the data of the non-magnetic isotopic polycrystalline sample$^{[12]}$ of LaGaO$_3$ by scaling the temperature according to the different molar masses of RCrO$_3$ and LaGaO$_3$ following the procedure proposed by Bouvier et al.$^{[22]}$

The magnetic entropy of CeCrO$_3$ gained by integrating $C_{mag}/T$ vs. $T$, is plotted in the inset in Figure 12. At low temperatures, the entropy amounts to $\sim R\ln 2$ indicating a doublet crystal field ground state of Ce$^{3+}$. Towards higher temperatures, the entropy captures contributions from excited crystal field states of Ce$^{3+}$ and contributions of Cr$^{3+}$ moment ordering. At the Néel temperature, the entropy reaches a value of $\sim R\ln 4$.

![Figure 12](image1.png)

**FIG. 12.** (color online) Temperature dependence of total heat capacities of Ce$_{1-x}$Eu$_x$CrO$_3$ ($x = 0.0$, 0.2, 0.5, 1.0). The inset shows the temperature dependence of magnetic entropy of CeCrO$_3$ ($x = 0.0$).

**D. Magnetic Neutron Scattering**

In order to determine the exact values of $T_N$, temperature dependent low-resolution high-intensity neutron powder diffraction patterns were carried out on several samples of Ce$_{1-x}$Eu$_x$CrO$_3$. Below the Néel temperature, all patterns exhibited a pronounced magnetic Bragg reflection near 2\(\theta\) $\sim$ 30.9° which can be indexed as (110)/(011). Additional, apparent magnetic scattering intensity was noticed for the (211)/(031) similar to what has been reported for CeCrO$_3$ by Shukla et al.$^{[19]}$. The integrated intensities of the (110)/(011) magnetic Bragg reflection are compiled in Figure 13 resulting in critical exponents, $\beta$, close to 0.34 in agreement with values expected for typical 3dim universality classes. None of the temperature traces for the different compositions reveals any signatures for re-orientation of the Cr moments at low temperatures associated to the anomalies observed in the magnetic susceptibilities (cf. Figure reference). SuceptZ(FC) indicating weak exchange coupling between the Ce moments. These rather orient readily in a stronger exchange fields of the Cr moments without a feed back.

![Figure 13](image2.png)

**FIG. 13.** (online color) Integrated intensity of the (110)/(011) magnetic Bragg reflection at 2\(\theta\) $\sim$ 30.9° vs temperature for various samples of Ce$_{1-x}$Eu$_x$CrO$_3$ as indicated. The inset shows the intensity versus the reduced temperature, $t = (T_N - T)/T_N$, where the critical temperature, $T_N$, for CeCrO$_3$ amounts to 258.1(1) K. The dashed line represents a critical power law $\propto t^{2\beta}$ with a critical exponent $\beta = 0.346(5)$.

**IV. DISCUSSION AND SUMMARY**

We have synthesized high-purity ceramic samples of Ce$_{1-x}$Eu$_x$O$_3$ where $x$ varied from 0 to 1. Extensive studies of the structural parameters by neutron and x-ray powder diffraction measurements reveal the dependence of antiferromagnetic ordering on details of the bonding angles and the lattice size. The effect of the cell decrease on the magnetic properties induced by substituting Eu for Ce appears to be rather indirect via a systematic change of Cr - O - Cr bonding and torsion angles which become necessary in order to accommodate
the rather rigid CrO₆ octahedra in the shrinking lattice. Substituting Eu for Ce in Ce orthochromites of composition Ce₁₋ₓEuₓCrO₃ not only rapidly decreases the Néel temperature of the antiferromagnetic ordering of the Cr³⁺ moments, but also gradually changes the thermal hysteresis behavior observed in the dc magnetization. In fact, samples with higher Eu content show a ZFC/FC splitting with a small peak in the FC susceptibility whereas the FC magnetization is reminiscent of the development of spontaneous magnetization in a ferromagnet. However, the saturation magnetization is far too low to account for the expected saturation magnetization of ∼3μB expected for Cr³⁺ with the spin S=3/2 moment. This finding rather indicates canted antiferromagnets as found e.g. for EuCrO₃.[12] Using high-resolution x-ray diffraction measurements with sufficient intensity up to d-values of ∼0.4 Å allowed us to reliably refine oxygen atom positions. From our structural investigation we concluded: (a) The cell volume decreases by ∼2.5% from CeCrO₃ to EuCrO₃ implying an overall increased density of Cr cations per unit volume for increasing Eu content. (b) Even though the cell volume reduction implies an overall increased density of Cr cations per unit volume, the Néel temperature decreases linearly with the Eu content. Figure 14 showing the Néel transition temperature of Ce₁₋ₓEuₓCrO₃ versus Eu content summarizes the results of all magnetic characterization measurements performed on the various phases studied in this work.

(d) Most striking, however, are the changes of the oxygen positions in the cell and the Cr - O - Cr bonding and torsion angles. The O1 atoms move considerably into the direction of the c - axis (∼5 %, cf. Fig. 10(a)) and one does not expect a marked alteration of the energies of the t₂g orbitals. The Cr - O2 distances (cf. Fig. 10(b) and (c)) exhibit a slight opposite dependence on the Eu content, however, their mean value exhibits only a very small, approximately linear increase by less than a percent. Accordingly, the “skewness” of the octahedra remains below ∼2° (cf. Fig. 8).

(c) Despite the decrease of the cell volume, the CrO₆ octahedra did neither shrink nor distort significantly. The Cr - O1 distances remain almost constant (cf. Fig. 10(a)) and one does not expect a marked alteration of the Néel temperature of rare-earth orthochromites.[12] They found that hydrostatic pressure essentially modifies bond distances and in turn leads to an increase of the Néel temperature whereas chemical pressure exerted by substituting a smaller rare-earth cation reduces the Néel temperatures by modifying antipolar displacements, Cr - O - Cr bond angles and the resulting oxygen octahedral tilts.[13]

(e) From the light to the heavier rare-earth elements Tₙ of RCrO₃ decreases by 60%. In terms of lanthanide contraction, the solid-solutions investigated in this work cover approximately half of the rare-earth series. By adjusting the Ce/Eu ratio, they allow to divide the interval between CeCrO₃ and EuCrO₃ into several small intervals which enables us to relate Tₙ with minute structural changes. Substituting Ce by the smaller Eu cations exerts chemical pressure. Using first-principles calculations Zhao et al. have estimated the effects of chemical pressure external versus hydrostatic pressure on the Néel temperature of rare-earth orthochromites.[13] They found that hydrostatic pressure essentially modifies bond distances and in turn leads to an increase of the Néel temperature whereas chemical pressure exerted by substituting a smaller rare-earth cation reduces the Néel temperatures by modifying antipolar displacements, Cr - O - Cr bond angles and the resulting oxygen octahedral tilts.[13]

The Néel temperatures decrease linearly with the Eu content following a Vegard’s-type dependence on the Eu concentration according to

\[ T_N = 260K - x \times 80K. \]

An analogous decrease of \( T_N \) induced by a decreasing cell volume across the whole series of the rare earth orthochromites has been observed before.[12][14] From the light to the heavier rare-earth elements \( T_N \) of RCrO₃ decreases by 60%. In terms of lanthanide contraction, the solid-solutions investigated in this work cover approximately half of the rare-earth series. By adjusting the Ce/Eu ratio, they allow to divide the interval between CeCrO₃ and EuCrO₃ into several small intervals which enables us to relate \( T_N \) with minute structural changes. Substituting Ce by the smaller Eu cations exerts chemical pressure. Using first-principles calculations Zhao et al. have estimated the effects of chemical pressure external versus hydrostatic pressure on the Néel temperature of rare-earth orthochromites.[13] They found that hydrostatic pressure essentially modifies bond distances and in turn leads to an increase of the Néel temperature whereas chemical pressure exerted by substituting a smaller rare-earth cation reduces the Néel temperatures by modifying antipolar displacements, Cr - O - Cr bond angles and the resulting oxygen octahedral tilts.[13]

(d) Most striking, however, are the changes of the oxygen positions in the cell and the Cr - O - Cr bonding and torsion angles. The O1 atoms move considerably into the direction of the c - axis (∼5 %, cf. Fig. 10(a)). Apparently, as a consequence of the decrease of the cell parameters and the cell volume and in order to keep the shape and size of the CrO₆ octahedra essentially unchanged, the Cr - O2 - Cr bonding angles decrease by ∼6 % (cf. Figure 10(a)). Simultaneously, the torsion angle O1 - Cr - O1 - Cr which measures to what extent neighboring CrO₆ octahedra are inclined with respect to each other increases by ∼25 % (cf. Figure 9(a)). The importance of bonding angles for the superexchange and the magnetic ordering has been investigated in detail by Zhou et al. for the RCrO₃ phases with emphasis on the heavy rare-earth elements and some light rare-earth R = La, Pr, Nd. In our investigation we have divided the range from CeCrO₃ to EuCrO₃, i.e. starting from a rare-earth element with a rather large ionic radius into several intervals and find analogous relationships between magnetic ordering and bonding and torsion angles. Especially the latter has been identified to be very essential for intrasite hybridization between Cr t and e orbitals. Intrasite hybridization lifts the t degeneracy and supports ferromagnetic coupling versus antiferromagnetic superexchange between the Cr - Cr moments.[12]

Finally we want to briefly comment on the crossing of the lattice parameters a and c (Figure 5) and the behavior of the positional parameters z0₁ and x0₁ of the
apical oxygen atoms (Figure 7) being different for small Eu levels, \( x \leq 0.04 \) from the behavior for \( x \geq 0.3 \). The intersection of \( a \) and \( b \) near \( x = 0.04 \) also reflected by the very small cell distortion factor (Figure 6) pointing to a lattice metrics close to cubic, seemingly indicating an attractive energy minimum which also pins the O1 atom positional parameters. Alternatively, a relaxation of lattice strain in the vicinity of the cubic metrics by random substitution of a substantially smaller Eu cation may also be taken into consideration to explain this observation.

In summary, our highly resolved x-ray powder and neutron powder diffraction measurements reveal that in the solid solutions \( \text{Ce}_{1-x}\text{Eu}_x\text{CrO}_3 \) the \( \text{CrO}_6 \) octahedra remain essentially rigid whereas \( \text{Cr} - \text{O} \) bonding and torsion angles change markedly by gradually substituting \( \text{Ce} \) by \( \text{Eu} \). Simultaneously, the Néel temperature decreases from 260 K to 180 K. As the \( \text{O}2 - \text{Cr} - \text{O}2 \) bond angle continuously moves away from 180° the torsion angles, which reflects to what extent the \( \text{Cr} - \text{O}2 - \text{Cr} \) bonds rotate out of the \( a - c \) plane when the size of the rare-earth ion is gradually reduced. This appears to constitute another determining parameter for magnetic ordering in the solid-solution phases \( \text{Ce}_{1-x}\text{Eu}_x\text{CrO}_3 \).

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