

Magnetoelastic Effect in Perovskite Orthochromite HoCrO_3

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It is well established that many material properties, such as multiferroicity, magnetoresistance, or magnetoelectricity, emerge from strong interactions of spins and lattice (phonons). An in-depth understanding of spin–phonon coupling is key to understanding these properties. We demonstrate strong spin–phonon coupling in HoCrO_3 using powder X-ray diffraction measurements. Our investigations confirm magnetoelastic effects below antiferromagnetic phase transition, $T_N \approx 142$ K. The lattice parameters and unit cell volume decrease normally with temperature up to $\sim T_N$, but decrease anomalously below T_N . By fitting the background thermal expansion for a non-magnetic lattice using the Debye–Grüneisen equation, we determined the lattice strain ΔV_M due to the magnetoelastic effects as a function of temperature. We have also established that the lattice strain due to the magnetoelastic effect in HoCrO_3 couples with the square of the ordered magnetic moment of the Cr^{3+} ion.

topics: perovskite, multiferroic, magnetostriction, X-ray diffraction

1. Introduction

The interaction between spin and lattice degrees of freedom is a subject of significant interest in condensed matter research, particularly in relation to electronic materials such as colossal magnetoresistive and multiferroic materials. One of the main manifestations of this coupling is the spontaneous exchange striction linked to magnetic ordering at low temperatures. In non-magnetic materials, the volume of the lattice unit cell varies smoothly with temperature and does not show any anomalous changes at low temperatures. However, in materials with magnetic ions ordering at low temperatures, atomic positions may change at the transition temperature. This leads to lattice strain, and as a consequence, one can expect modifications in the unit cell parameters, unit cell volume, and sometimes lattice symmetry. To determine these anomalous changes effectively, high-resolution diffraction measurements are required, preferably in an extended temperature range above and below the magnetic ordering temperature. This enables a precise determination of phonon-related lattice contraction, which can be subtracted from experimental data to determine excessive changes in lattice parameters due to magnetic ordering.

Perovskite chromites RCrO_3 (R = rare-earth or yttrium) have been reconsidered in recent years as possible multiferroic materials in which multiple ferroic orders, such as ferroelectricity and antiferromagnetism, coexist [1–3]. These perovskites are isostructural with rare-earth orthoferrites RFeO_3 and crystallize in an orthorhombically distorted perovskite structure with four formula units per unit cell [4]. Orthochromites are paramagnetic at room temperature and magnetically ordered at low temperatures [5–7]. In the case of orthochromite HoCrO_3 , upon cooling from room temperature, the Cr magnetic sublattice is ordered at $T_N \approx 142$ K, whereas cooperatively induced magnetic ordering of the Ho sublattice was observed at much lower temperatures, $T < 50$ K [8]. Based on a systematic rare-earth site doping study, it was concluded that HoCrO_3 shows a strong correlation between crystal structure and magnetism [9]. From our earlier neutron powder diffraction (NPD) studies, we were able to point out the anomalous change in the unit cell volume below T_N [8] in this compound, but the temperature evolution of the anomalous changes was not clearly determined around T_N . This was due to a limited number of NPD data sets as a function of temperature around T_N . Furthermore, the previous report lacked the high-temperature data required

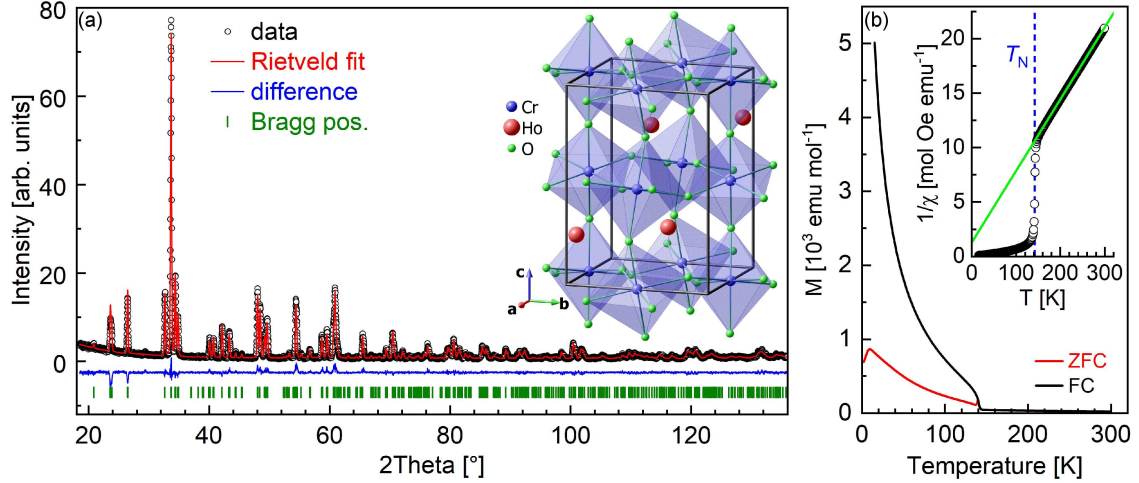


Fig. 1. (a) Powder X-ray diffraction pattern collected at 298 K along with Rietveld refinement results. Circles are the experimentally measured intensities, and the solid line (red) is the curve obtained by Rietveld fitting. Vertical bars (green) mark the positions of expected Bragg reflections. The blue horizontal curve at the bottom is a difference between the measured and calculated patterns. The inset shows a clinographic view of a lattice unit cell along with distorted Cr–O octahedra. (b) The zero-field-cooled (ZFC) and field-cooled (FC) magnetization measured under 500 Oe applied field shows a bifurcation around 142 K, indicating the magnetic transition. The inset shows the Curie–Weiss fit to inverse susceptibility, which unambiguously shows the deviation of the experimental curve below 142 K indicated by the vertical dashed line.

TABLE I

Structural parameters for HoCrO_3 obtained from the Rietveld refinement of powder XRD data collected at 298 K.

Atom	Site	Occ.	x	y	z
Ho	4c	1	-0.0178	0.0651	0.25
Cr	4b	1	0.5	0	0
O(1)	4c	1	0.097	0.473	0.25
O(2)	8d	1	0.695	0.297	0.0478

for a better evaluation of structural changes around and below the magnetic phase transition. The current study, which includes much denser data sets around T_N , as well as high-temperature data (up to 998 K), has enabled us to determine the spin-lattice coupling in these compounds more precisely.

2. Experimental details

A polycrystalline sample of HoCrO_3 was synthesized by a conventional solid-state chemical reaction of Ho_2O_3 and Cr_2O_3 in a stoichiometric ratio. The precursors were mixed using an agate ball mill and heat-treated at 1100°C for 48 h in the presence of atmospheric air. Further details of the synthesis can be found in [10]. The phase purity of the synthesized powder sample was then confirmed by powder X-ray diffraction (PXRD) measured on a Panalytical Empyrean powder diffractometer with a $\text{Cu } K_\alpha$ radiation source. Measurements were done using Bragg–Brentano geometry on finely powdered

samples. After confirming the phase purity, several PXRD patterns were collected in a wide temperature range of 9–998 K. The diffraction patterns were analyzed by the Rietveld method using the software Mag2Pol [11]. The magnetization of the polycrystalline HoCrO_3 sample was measured by a Quantum Design superconducting quantum interference device magnetometer in the temperature range from 2 to 300 K under the magnetic field 500 Oe.

3. Results and discussion

The Rietveld refinement results of the PXRD data at 298 K are presented in Fig. 1a. Inset in Fig. 1a shows a clinographic view of a refined crystal structure using the orthorhombic space group $Pbnm$. This orthorhombically distorted perovskite structure contains four formula units of HoCrO_3 per unit cell. The refined lattice and structural parameters at 298 K are displayed in Table I. The field-cooled (FC) and zero field-cooled (ZFC) direct current (DC) magnetization curves measured with an applied magnetic field of 500 Oe presented in Fig. 1b show a bifurcation around ~ 142 K. It is attributed to the magnetic ordering of the Cr^{3+} sublattice [7, 8, 12]. The thermal evolution of reciprocal susceptibility calculated from the FC magnetization curve is presented as inset in Fig. 1b. The inverse susceptibility follows the Curie–Weiss law above T_N , and there is a marked deviation below T_N , as shown in the inset of Fig. 1b. From the Curie–Weiss fit of the magnetic susceptibility, the effective moment is found to be $11.01 \pm 0.02 \mu_B$, which is very similar to

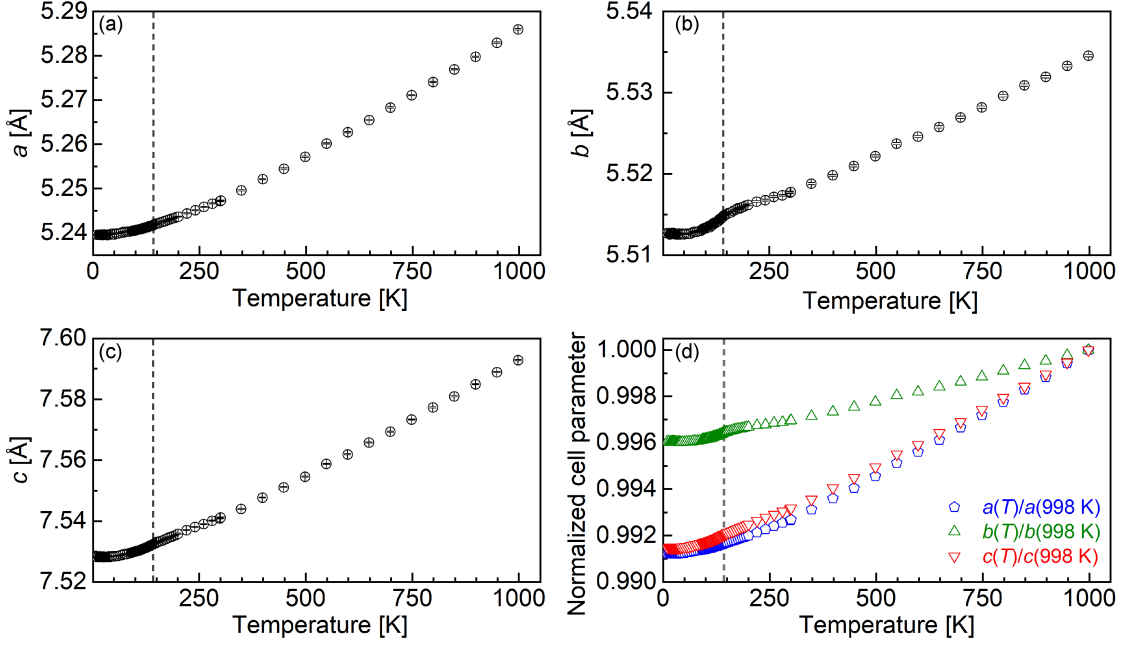


Fig. 2. Panels (a), (b), and (c) show the temperature evolution of lattice parameters a , b , and c , respectively. The Néel temperature $T_N = 142$ K is indicated by vertical dashed lines. Panel (d) shows the lattice parameters normalized to the value obtained at 980 K.

the value from the earlier report [8]. By considering the theoretical values $3.87 \mu_B$ for Cr^{3+} (for the spin only $S = 3/2$) and $10.63 \mu_B$ for Ho^{3+} ($J = 8$) and assuming that the total effective magnetic moment is given by $\mu_{\text{total}} = [\mu_{\text{eff}}^2(\text{Cr}^{3+}) + \mu_{\text{eff}}^2(\text{Ho}^{3+})]^{1/2}$, we expect a total magnetic moment of $11.31 \mu_B$. Thus, the experimental effective magnetic moment is very close to the expected value.

To determine the structural changes and to elucidate their relation to magnetic order, diffraction data was collected in the temperature range 9–998 K. Refinements of the diffraction patterns in the whole temperature range indicated no structural transition, and the structure remained orthorhombic $Pbnm$. Figure 2a–c shows the variations of lattice parameters a , b , and c . The variations of lattice parameters with temperature do not show discontinuous changes, but all three lattice parameters show an anomalous change below $\sim T_N$, indicated by a vertical dashed line in the figure. It is worth noting that from the normalized values of temperature evolution of the lattice parameters presented in Fig. 2d, the reduction in the lattice parameter b as a function of temperature is much smaller compared to the reductions in a and c . This indicates that b is relatively stiff compared to the other two crystallographic axes. The anomalies observed in lattice parameters affect the unit cell volume of HoCrO_3 . As shown in Fig. 3, the unit cell volume also shows anomalous change below T_N . In order to elucidate the excessive change in the volume of the unit cell due to magnetoelastic effects, it is necessary to determine expected changes in the volume of the lattice cell in the absence of

a magnetic phase transition. One way to determine the background temperature variation of lattice parameters and unit cell volume is to extrapolate the temperature variation of these parameters in the paramagnetic phase down to low temperatures by fitting them with a polynomial function [13]. This method works approximately in some cases, but in general, it involves some uncertainty. Alternatively, one can use the Grüneisen approximation for the zero-pressure equation of state, in which the effects of thermal expansion are considered to be equivalent to elastic strain [14, 15]. Thus, the temperature dependence of the volume can be described by

$$V(T) = \frac{\gamma}{B}U(T) + V_0, \quad (1)$$

where γ is a Grüneisen parameter, B is the bulk modulus, and V_0 is the unit cell volume at $T = 0$ K in the absence of magnetoelastic effect. The internal energy, $U(T)$, can be obtained via a Debye approximation for the heat capacity, i.e.,

$$U(T) = 9Nk_B T \left(\frac{T}{\theta_D} \right)^3 \int_0^{\theta_D/T} dx \frac{x^3}{e^x - 1}, \quad (2)$$

where N is the number of atoms in the unit cell, k_B is Boltzmann's constant, θ_D is the Debye temperature, and $x = \hbar\omega/(k_B T)$. The experimental unit cell volume was fitted to (1) along with (2) in the paramagnetic temperature range $150 < T < 998$ K. The fitting parameters V_0 , θ_D , and $9Nk_B \frac{\gamma}{B}$ were determined through a least-squares fitting procedure. The determined parameters are presented in Table II. The resulting fit that describes the evolution of the unit cell volume in the absence of

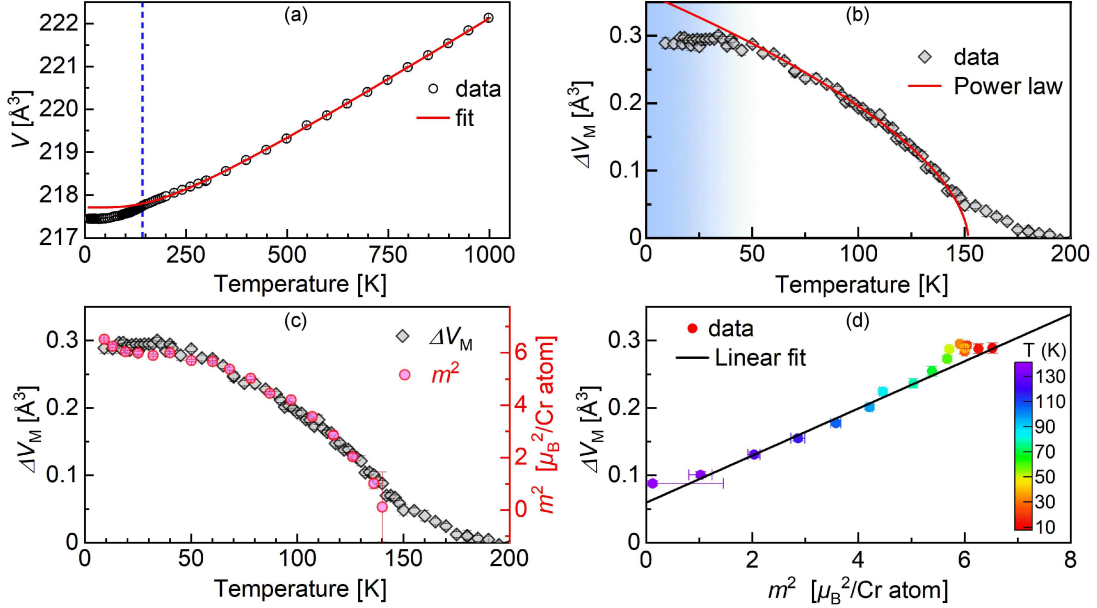


Fig. 3. (a) Temperature evolution of the unit cell volume obtained from diffraction measurements (circles) and fit using the Grüneisen approximation presented in (1) (line). (b) Temperature evolution of excessive change in the unit cell volume ΔV_M fitted to a power-law. The changes in ΔV_M saturates below 50 K, where Ho^{3+} ordering becomes dominant. (c) Temperature evolution of excessive change in the unit cell volume ΔV_M (left scale) and square of the ordered Cr^{3+} magnetic moments (m^2) (right scale). (d) The excessive change in the unit cell volume plotted against m^2 at several temperatures. The inset color bar indicates the temperature range of experimental data points.

magnetic ordering is shown as a solid line in Fig. 3a. A clear deviation between the fit and experimental data was observed slightly above $T_N = 142$ K. It can be inferred that this is an indication of strong magnetostriction or magnetoelastic effects in this system. The volume change due to magnetoelastic effects is expected to be proportional to the square of the ordered magnetic moment [16]. The excessive change in the unit cell volume due to magnetoelastic effects, ΔV_M , presented in Fig. 3b, was revealed by taking the difference between the experimental unit cell volume and the fit to Grüneisen approximation. The results ΔV_M follow a power-law given by the expression $\Delta V_M(T) = \Delta V_M(0) (T_N - T/T_N)^\beta$. Here, $\Delta V_M(T)$ is the temperature evolution of ΔV_M ; $\Delta V_M(0)$ is ΔV_M at 0 K; T_N and β are the Néel temperature and the critical exponent, respectively. From the fit shown as a continuous curve in Fig. 3b, we obtained $T_N = 151 \pm 3$ K and the critical exponent $\beta = 0.57 \pm 0.07$. The thus obtained T_N is in agreement with magnetic data. A small deviation of power-law fit can be observed below 50 K, which coincides with the temperature at which magnetic ordering of the rare-earth Ho^{3+} sub-lattice is observed [8]. In Fig. 3c, we present ΔV_M along with the square of the ordered magnetic moment of the Cr^{3+} ion, obtained by neutron diffraction experiments [8]. It is immediately clear from Fig. 3c that excessive changes in the unit cell volume follow the ordered magnetic moments of the Cr^{3+} ion. In Fig. 3d, ΔV_M is plotted against a square of the Cr^{3+}

TABLE II

The results of least-squares fitting using Grüneisen approximation (see (1)).

V_0 [\AA^3]	θ_D [K]	$9Nk_B \frac{\gamma}{B}$ [$\text{\AA}^3/\text{K}$]
217.75(1)	732(11)	0.0178(1)

ordered magnetic moments at several temperatures, showing a linear relation. This unambiguously confirms that the anomalous change in lattice parameters and unit cell volume in HoCrO_3 is due to spontaneous magnetostriction or magnetoelastic effects.

4. Conclusions

We have investigated spontaneous magnetoelastic effects or magnetostriction in HoCrO_3 by means of powder X-ray diffraction in an extended temperature range. The results of our investigation show that all lattice parameters and unit cell volume exhibit an anomalous change below $T_N = 142$ K. By subtracting the background thermal expansion for a non-magnetic lattice, we determined the lattice strain ΔV_M due to magnetoelastic effects as a function of temperature below T_N . We also show that the lattice strain due to spontaneous magnetostriction in HoCrO_3 couples with the square of the ordered magnetic moment of the Cr^{3+} ion.

Acknowledgments

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