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Mechanism of exchange striction of ferroelectricity in multiferroic orthorhombic HoMnO_3

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Abstract. *E*-type perovskite magnet HoMnO_3 is considered a prototype Mn-Mn exchange-striction driven multiferroic. We have, for the first time, grown orthorhombic HoMnO_3 single crystals, and studied the directional dependence of its electric polarization \mathbf{P} . The direction of \mathbf{P} is not along the crystallographic a axis, as predicted, but along the c axis. The magnetic state is incommensurate. \mathbf{P} along the c axis is primarily induced by Ho-Mn exchange striction, and Mn-Mn striction in the incommensurate spin state leads to an antiferroelectric order along the a axis. We predict the rotation of \mathbf{P} with temperature in commensurate *E*-type RMnO_3 (R =magnetic rare earth).

Multiferroics attract significant attention because of cross-coupling between magnetism and ferroelectricity (FE), and the related possibility of controlling magnetism with an electric field (and vice versa) [1,2]. FE induced by magnetic order is especially interesting because of the strong effect of a magnetic field (H) on the ferroelectric order. Exchange striction is a major mechanism producing FE in magnetically ordered systems [2]. Both symmetric and antisymmetric parts of the exchange coupling can drive FE. The latter case is known to occur in spiral magnets, such as TbMnO_3 [2]. These systems exhibit small electric polarizations (\mathbf{P}) of the order of $10^{-1} \mu\text{C}/\text{cm}^2$ – three orders of magnitude smaller than in proper ferroelectrics. Symmetric exchange is expected to produce much larger \mathbf{P} . However, the corresponding materials identified so far show similarly small values of \mathbf{P} [3,4]. Theoretical predictions [5,6] of a 100 times larger \mathbf{P} in the magnetic E -phase of orthorhombic perovskite manganites $\text{o-}R\text{MnO}_3$ ($R=\text{Ho-Lu}$, and Y) induced by Mn-Mn exchange striction has, therefore, attracted a lot of interest [7-10]. Unfortunately, these compounds exhibit [9,10] maximum \mathbf{P} values of only $\sim 10^{-1} \mu\text{C}/\text{cm}^2$. In many cases (*e.g.* for $R=\text{Ho}$), any significant \mathbf{P} is achieved only below the rare earth magnetic ordering temperature (T) [9]. This indicates an essential role of the rare earth magnetism, which is unaccounted for in the extant models. Importantly, all the E -type manganites studied so far have been only synthesized in the polycrystalline form, preventing characterization of many of their intrinsic properties.

In this paper, we report the studies on single crystals of orthorhombic HoMnO_3 (o-HoMnO_3). Unexpectedly, we find that \mathbf{P} is pointing along the crystallographic c axis, contrary to the theoretical prediction [5,6] of $\mathbf{P} \parallel a$. We argue that Ho-Mn exchange striction plays a key role in this system, and discuss possible outcomes of the Mn-Mn interaction in the orthorhombic manganites. Our model predicts that in magnetic rare earth manganites, coexisting Mn-Mn and R -Mn interactions can give rise to a distinctive phenomenon – a temperature-dependent direction of \mathbf{P} .

o-HoMnO₃ crystallizes in a distorted perovskite structure (space group $Pbnm$), shown in Fig. 1(a). We have synthesized rod-like large single crystals with dimensions up to 2x2x7 mm³ (see Fig. 1(b)) utilizing conventional Bi₂O₃ flux method. Previously, polycrystalline o-HoMnO₃ has been obtained using high-pressure synthesis. We find that flux growth with Bi₂O₃, Ho₂O₃ and MnO₂ can stabilize both hexagonal *and* orthorhombic crystals at the ambient pressure. Mixture of Bi₂O₃:Ho₂O₃:MnO₂ = 6:0.5:1 ratio produces the hexagonal phase, whereas 12:0.5:1 ratio leads to orthorhombic single crystals. The crystals exhibit an orthorhombic perovskite structure with $a=5.2689(2)$, $b=5.8450(2)$, and $c=7.3698(2)$ Å at room temperature, and no twinning, as confirmed by refinement of single-crystal x-ray diffraction data. It is consistent with previously published structure of polycrystalline samples [11,12]. The absence of twinning was further confirmed by neutron diffraction experiments, in which a careful search revealed no diffraction peaks due to possible twin domains. Magnetization (M) was measured with a SQUID magnetometer. P and dielectric constant (ϵ) were obtained by integrating pyroelectric current measured with an electrometer and using an LCR meter at $f=44$ kHz, respectively. Neutron diffraction data were collected on BT9 triple-axis spectrometer at NIST Center for Neutron Research.

Mn spins in o-HoMnO₃ order at $T_N \approx 40$ K, exhibiting $(0, A_y, 0)$ -type incommensurate structure with wave vector $Q=(h,k,l)=(0, \sim 0.4, 0)$, and spins parallel to the b axis [11]. At a lower T , *some* polycrystalline samples [12] become commensurate with $k=0.5$, exhibiting the E -type order discussed theoretically in Ref. [5], and shown in Fig. 1(a). For $T < 15$ K, Ho spins order in the $(a_x f_y, 0)$ pattern and the same Q as Mn [11]. Our data are consistent with these results. Magnetic field (H) and T dependences of M are shown in Figs. 1(c,d). The anomalies corresponding to $T_N=42$ K and $T_{Ho}=15$ K are clearly observed in the T derivative of M_c shown in the inset in Fig. 1(d), as well as in the M_a and M_b derivatives (not shown). At low T , substantial magnitude of M_b develops, possibly due to Ho contribution. Fig. 2 shows T dependence of various physical properties under zero H . Onset of tiny ferroelectric polarization along the c axis (P_c) at $T=30$ K appears (Fig. 2(a)), and P_c exhibits an abrupt increase at $T_{Ho}=15$ K, reaching 1,500 $\mu\text{C}/\text{m}^2$ at 2 K. The magnitudes of P_a and P_b are

negligible at any T . Dielectric constant along the c axis (ϵ_c) displays a pronounced peak at T_{Ho} , in accordance with the appearance of FE, whereas ϵ_a increases broadly below T_N , see Fig. 2(b). The specific heat, shown in Fig. 2(d), exhibits a sharp peak at T_N , and a small (but discernable) anomaly at T_{Ho} is also visible.

Neutron diffraction data show that our samples are incommensurate at all temperatures. Fig. 2(c) shows the T dependence of the integrated intensity of the $(0, k, 1)$ magnetic peak, $k \approx 0.4$. The magnetic order appears at $T_N = 42$ K, and the peak intensity increases significantly for $T < T_{Ho}$, simultaneously with a large increase of P_c . Inset in Fig. 2(c) shows the T -dependent position k of the magnetic peak obtained from Gaussian fits. With decreasing T , k exhibits a slight variation, but always stays close to $k = 0.4$. There appear to be changes in the slope of this dependence in the vicinity of the FE anomalies at ~ 30 K, and at 15 K, reflecting the magnetoelectric coupling in this system.

The FE in the E -type manganites is currently believed [5,6] to be induced by Mn-Mn symmetric exchange striction, *i.e.* repulsion of co-aligned Mn spins. This repulsion, together with the associated motion of the oxygen ions, leads to the appearance of P_a , as illustrated in Fig. 1(a) for the $k = 0.5$ commensurate state. The Mn spin is given by $S_y(y) = S \cos(ky - \varphi_l)$, where φ_0 and $\varphi_{1/2}$ are the phases for the two spin chains along the b axis in the unit cell, one at $x = 0$, and the other at $x = 0.5$ (x, y are in lattice units), see Fig. 3(a). In the E -type commensurate state, $k = 0.5$, $\Delta\varphi = \varphi_{1/2} - \varphi_0 = \pi/2$, and the magnetic structure lacks the inversion symmetry, *i.e.* is acentric. Superimposed on the lattice structure, it is consistent with non-zero P_a . In the $k \neq 0.5$ state the spin magnitude is not constant, and other phase differences $\Delta\varphi$ are allowed, leading to both polar acentric (*e.g.* $\Delta\varphi = \pi/2$), and centric ($\Delta\varphi = 0$ and π) spin density waves (SDW).[13] In the latter case, $P_a = 0$ if the inversion centers of the SDW and the atomic structure coincide. In our samples, measured P_a is zero, and therefore the centric incommensurate SDW must be realized. One of the two possible Mn magnetic structures for the centric incommensurate SDW, corresponding to $\Delta\varphi = 0$, is shown in Fig. 3(a), the other with $\Delta\varphi = \pi$ simply has the opposite spin direction for $x = 0.5$.

(For simplicity, the $k=0.4$ state with period of exactly 5 unit cells is shown.) These structures are antiferroelectric, with one half of the unit cell having the opposite P_a to the other. Large increase of ϵ_a below T_N (Fig. 2) without the presence of P_a strongly supports this conclusion.

The primary result of our work is the unexpected direction of \mathbf{P} . Because of the clear association of FE with the Ho order, the natural candidate mechanism of multiferroicity is Ho-Mn interaction. In fact, rare-earth – 3d element interaction was reported to be essential in multiferroic orthoferrites [14,15], as well as to play a role in some spiral manganites [16,17]. We find that Ho-Mn exchange striction indeed provides a simple explanation for the observed phenomena. Disregarding the x component of the Ho spins which does not contribute to the striction, the Ho SDW order essentially follows that of Mn, but with an experimentally undetermined phase shift between the two [11]. To maximize the energy gain from the Ho-Mn striction producing the c -axis displacement, the phase shift should be zero or π because it pairs large Ho and Mn spins adjacent in the x direction (the Mn spins adjacent in the y direction are antiparallel to each other for the same z , partially cancelling the effect of the striction). As shown in Fig. 3(b) for one of these phase shifts, the Ho spin is then anti-aligned with the 3 Mn spins below, and aligned with the 3 Mn spins above, and moves down due to exchange striction. One can readily check that in this case, Mn-Ho exchange striction moves all the Ho spins of one chain (*e.g.* for $x=0$) in the same direction along the c axis. The energy gain is the same for aligning with the Mn spins above or below the Ho atom, and therefore the $x=0$ and $x=0.5$ Ho chains in the magnetic unit cell can either have the same or the opposite directions of P_c . Experimentally, $P_c \neq 0$, and therefore the Ho order shown in Figs. 3(a,b) which produces the same P_c in every Ho chain should be realized. Clearly, experimental confirmation of this phase relationship between the Ho and Mn SDWs, and whether it is affected by the poling used for P_c measurements, would be of significant interest. Finally, we note that the onset of the weak P_c at $T \approx 30$ K could be produced via the same mechanism due to weak Ho moment induced by the Mn order, which was previously observed in polycrystalline samples [12].

o-HoMnO₃ exhibits a strong magnetoelectric effect. Fig. 4(a) shows the full suppression of P_c at $H=2$ and 4 T for $H||b$ and $H||a$, respectively. For $H||c$, only a small decrease of P_c is found. The suppression of P_c coincides with a drop in ϵ_c (Fig. 4(b)), and with an anomaly in dM/dH (inset in Fig. 4(a)). The vanishing polarization is probably associated with field-induced reorientation of the Ho spins and the corresponding changes in the effects of Ho-Mn exchange striction. Our data show that the reorientation is easier to achieve in the ab plane, consistent with the magnetic anisotropy that tends to confine the Ho spins there [11,12]. Figs. 4(c-h) show T dependences of P_c and ϵ_c in various applied fields. Consistent with the data of Figs. 4(a,b), magnetic field suppresses the ferroelectric state, and decreases the ferroelectric transition temperature.

Presence of two coexisting exchange-striction mechanisms of multiferroicity in the E-type orthorhombic manganites is the key result of this work. Depending on the phase relationships within and between the Mn and Ho SDWs, both Mn-Mn and Ho-Mn interactions can produce zero or non-zero electric polarization along the a and c axis, respectively. The $k=0.5$ state appears to be an exception for which the $P_a=0$ state is absent, because centric SDW would imply zero Mn spin for half of the Mn ions. However, even for $k=0.5$, states with both zero and non-zero P_c are possible, as illustrated in Fig. 3(c). The presence of two coexisting mechanisms producing different directions of \mathbf{P} may open possibilities for distinctive magnetoelectric control, and should lead to previously unobserved phenomena. In our samples, only one mechanism (Ho-Mn) leads to FE. However, some of the previously studied polycrystalline o-HoMnO₃ samples [12] enter the $k=0.5$ state at $T=T_L$ which is larger than T_{Ho} , and significant \mathbf{P} is observed for $T_{Ho}<T<T_L$. A large increase of \mathbf{P} at T_{Ho} is also present in these samples. For these samples, our model predicts that the polarization is initially along the a axis, and that a large c -axis component develops in addition with decreasing T . Thus, we expect that the *direction* of \mathbf{P} changes with T in the $k=0.5$ crystals. The reason for the variation of the exact magnitude and T dependence of \mathbf{P} and (in)commensurability among published results in polycrystalline

specimens [11,12] and our crystal data is currently unclear, but the presence of defects or residual strains may play an important role. To verify the intriguing possibility of temperature-induced rotation of the \mathbf{P} , preparation of such $k=0.5$ crystals is certainly desirable.

In summary, we report studies of single-crystalline o-HoMnO₃, which is currently considered a prototype *E*-type multiferroic with symmetric exchange-striction mechanism. Contrary to the current belief, the ferroelectric polarization in our crystals is along the *c* axis. We argue that Mn-Mn and Ho-Mn exchange striction mechanisms coexist in this system. These mechanisms can lead to both ferroelectric and antiferroelectric orders along the *a* axis (Mn-Mn), and the *c* axis (Ho-Mn). In our samples, the Ho-Mn interaction produces the *c*-axis polarization, while the Mn-Mn exchange striction induces the *a*-axis antiferroelectric order. We also propose that under certain conditions, these coexisting mechanisms should lead to temperature-induced rotation of FE polarization in the *E*-type manganites.

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Figure Captions.

FIG. 1 (a) Lattice and magnetic structure ($k=0.5$) of *E*-type orthorhombic $RMnO_3$. *R* atoms are not shown. Oxygen displacements reflect the effect of Mn-Mn exchange striction. Dashed line shows structural unit cell. The magnetic unit cell is twice as large in the *y* direction. (b) Single crystal of o-HoMnO₃. (c) Magnetization vs. magnetic field for $T=2$ K. (d) Magnetic susceptibility vs. temperature ($1 \text{ emu}=4\pi\cdot 10^{-6} \text{ m}^3$). The inset shows

temperature derivative of the susceptibility.

FIG. 2 Temperature dependences of the electric polarization (a) and dielectric susceptibility (b) along the three crystallographic axes. (c) Integrated intensity of the (0, k ,1) magnetic peak vs. temperature. The k component of the peak position is shown in the inset. (d) Temperature dependence of the specific heat.

FIG. 3 (a), (b) The magnetic order leading to $P_a=0$ and $P_c>0$ in the $k=0.4$ state. Dashed line in (a) outlines the magnetic unit cell. In (b), thick solid and dashed lines designate attractive and repulsive Ho-Mn interactions, respectively. (c) Spin structures with zero and non-zero c -axis polarization in the $k=0.5$ E -type state. In all figures, the a -axis components of the Ho spins are not shown.

FIG. 4 Magnetic field dependences of the electric polarization P_c (a) and dielectric susceptibility ϵ_c (b) for different directions of H . Temperature dependences of the electric polarization (c-e), and the dielectric susceptibility (f-h) in various applied magnetic fields.

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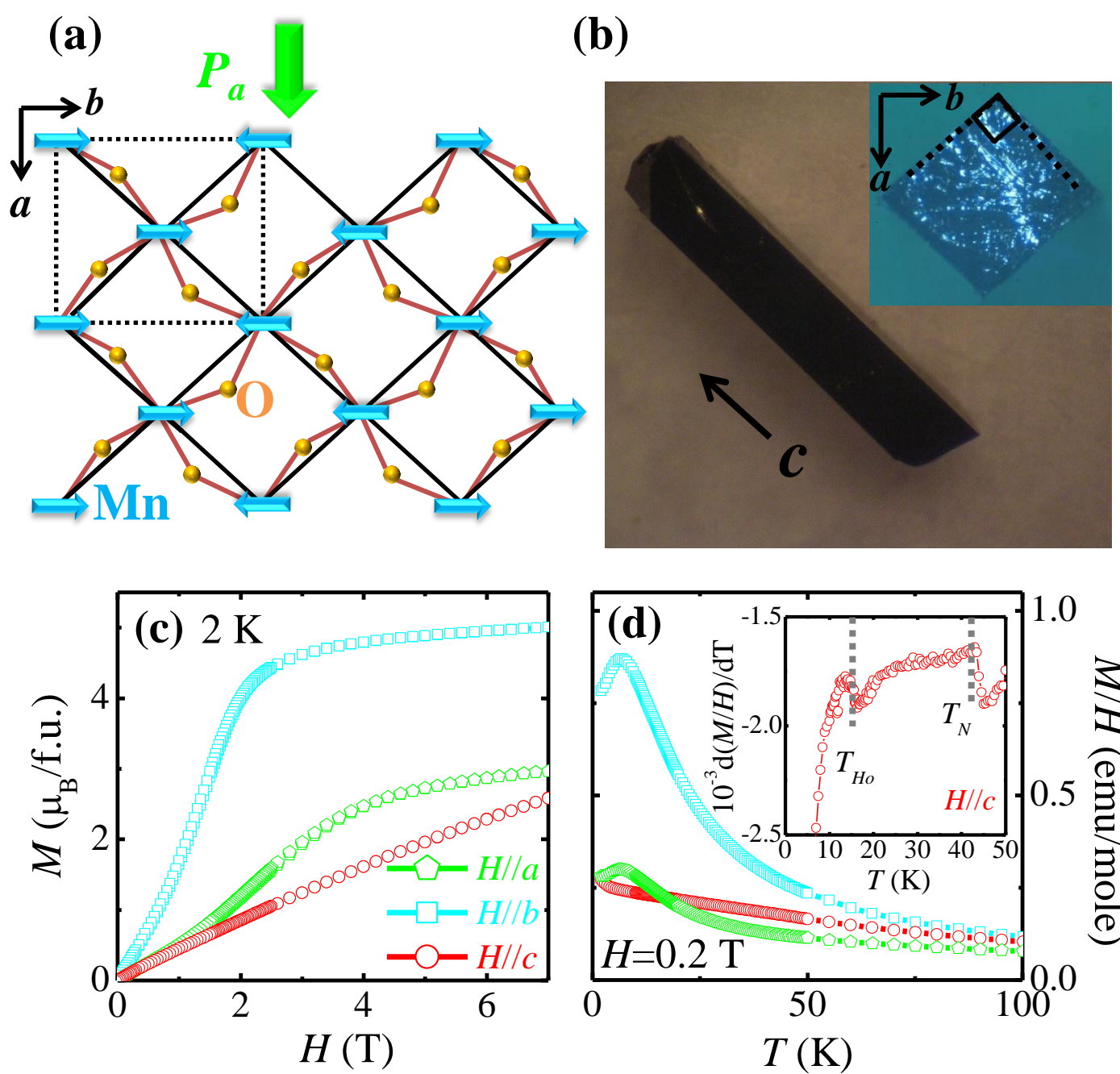


Figure 1 N. Lee *et al.*

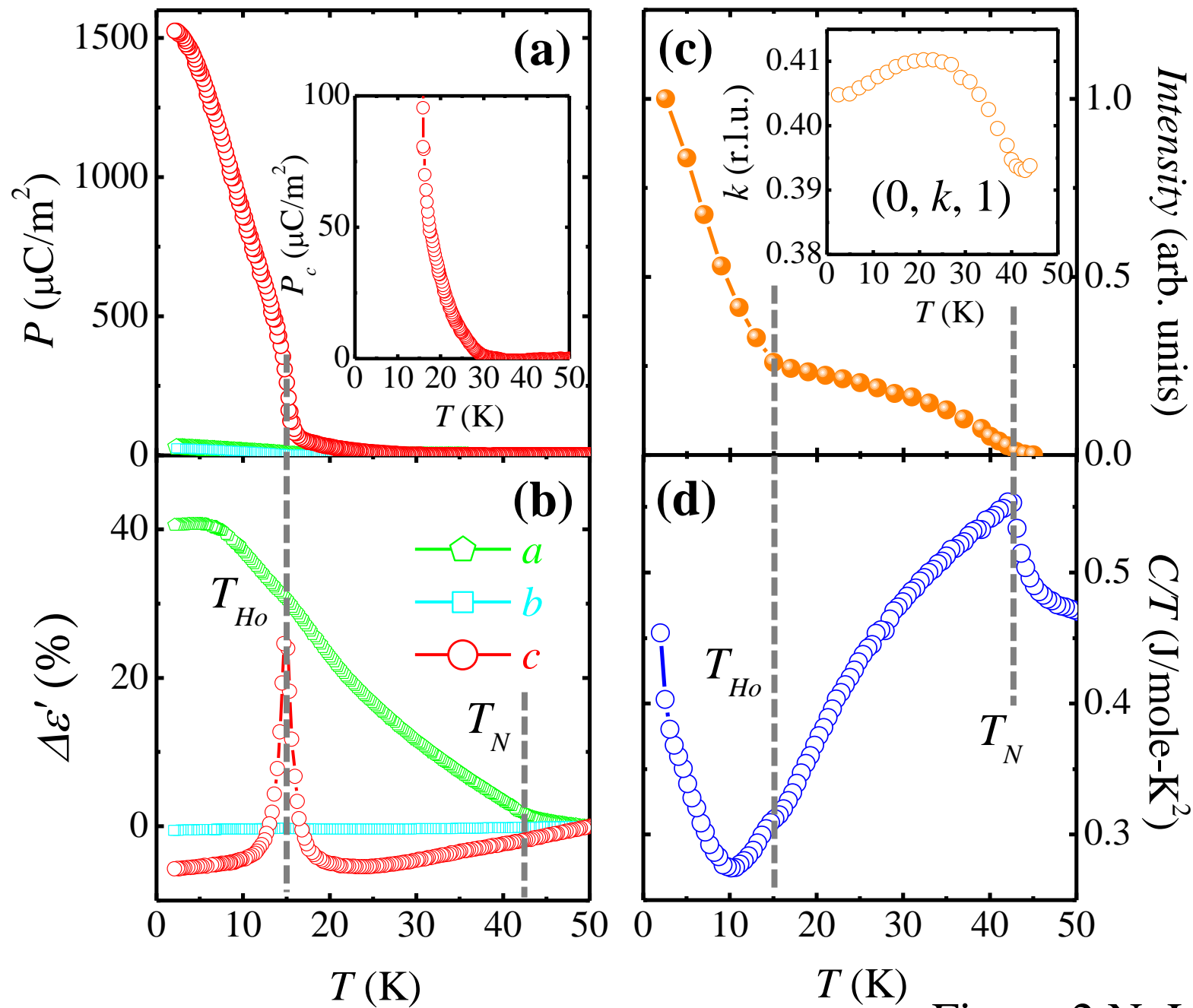


Figure 2 N. Lee *et al.*

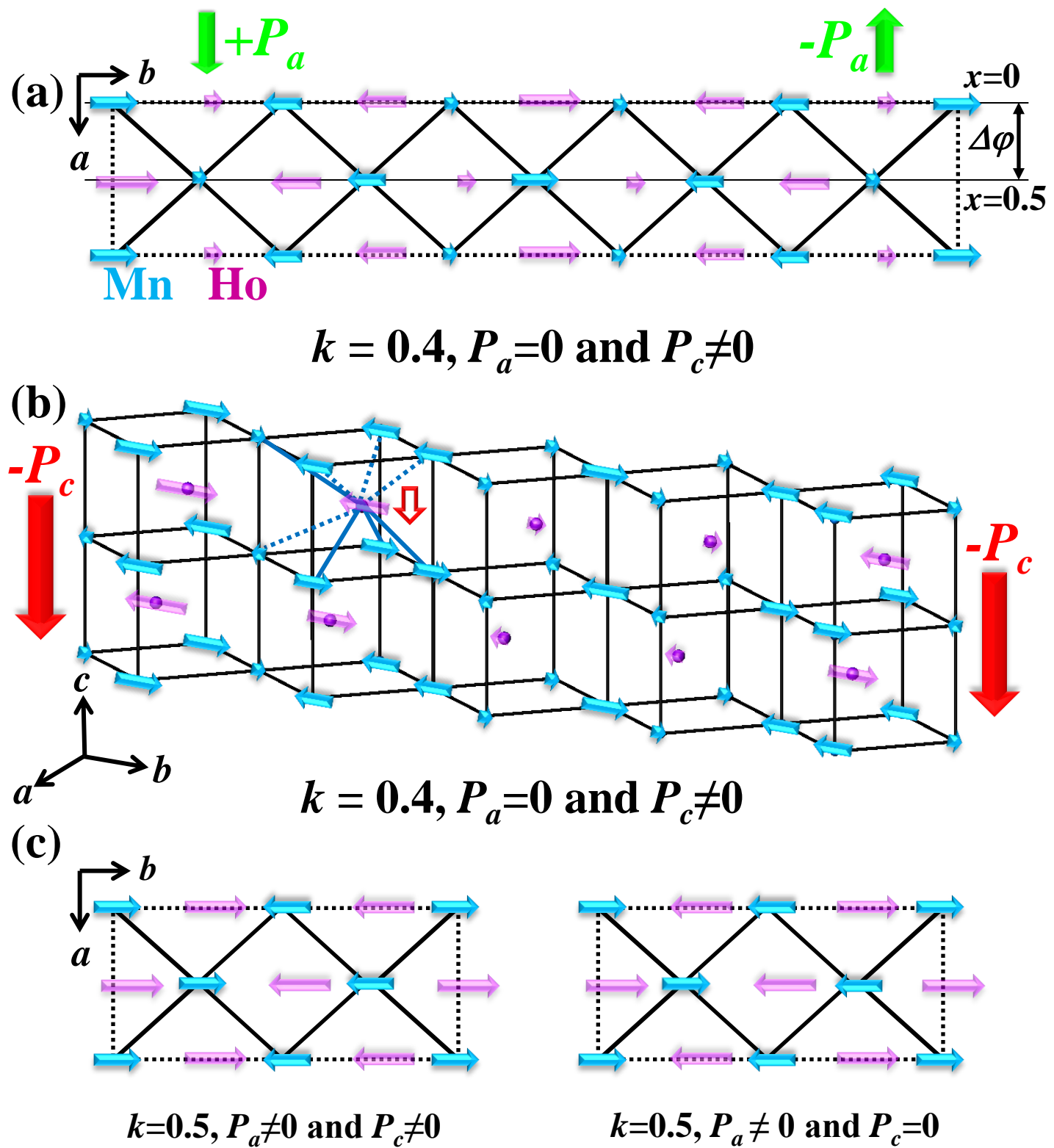


Figure 3 N. Lee *et al.*

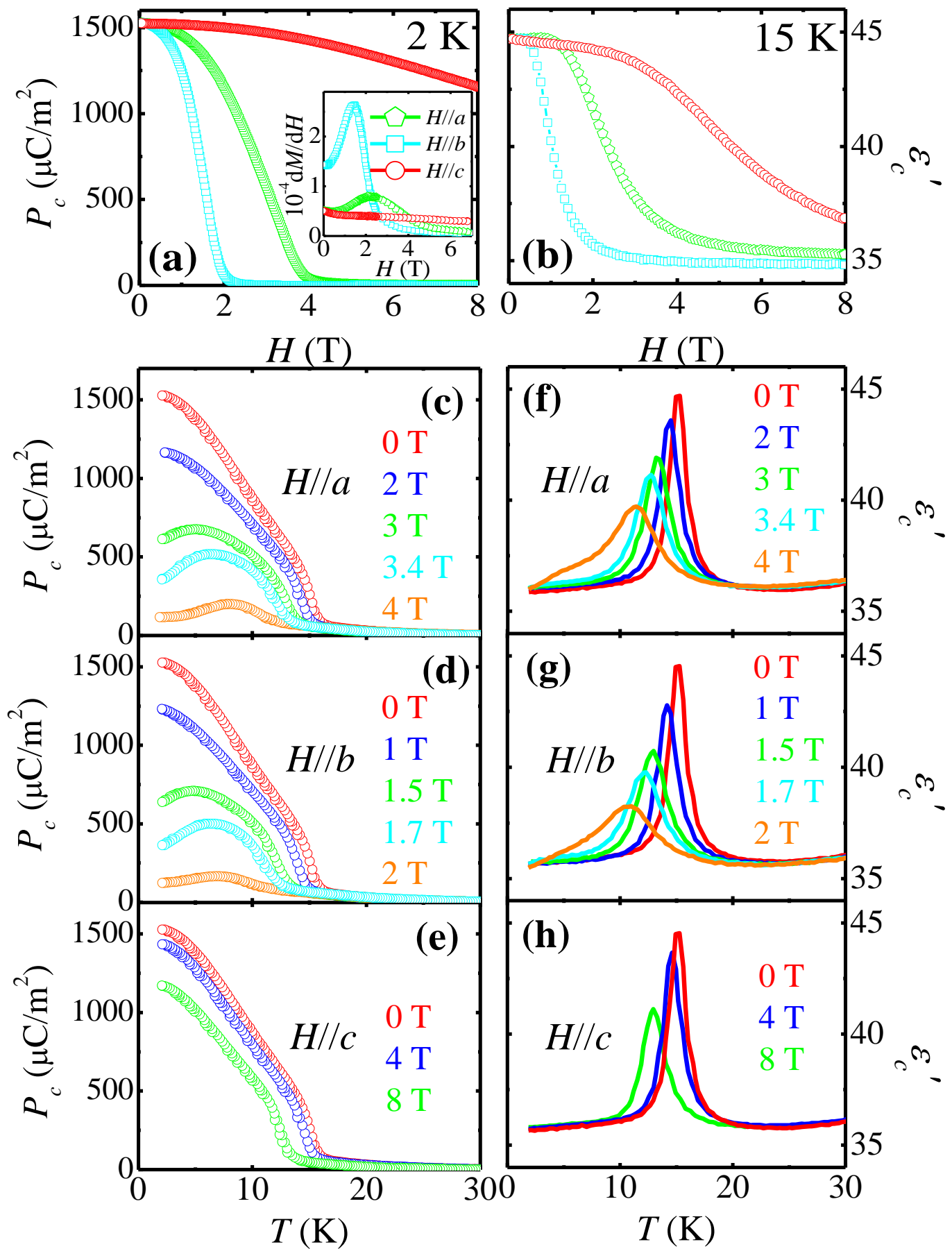


Figure 4 N. Lee *et al.*