Magnetostriction in a simple trivalent manganese perovskite

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We found an unusual negative thermal expansion in the simple perovskite MnF_3 below the Neel point, where the spins are ordered in an A-type magnetic structure. The structure of MnF_3 has been studied between 5 and 500 K using powder neutron and synchrotron diffraction. The structure remains monoclinic $C2/c$ over the entire temperature range. We have found that the interplay of spin and orbital ordering is sufficient to result in a large positive magnetovolume effect without charge ordering. This expansion is reminiscent of the Invar effect observed in certain alloys.

The observation of colossal magneto resistance (CMR) in oxides derived from the simple manganese perovskite $LaMnO_3$ has prompted numerous studies of this phenomenon and is an elegant demonstration of the importance of competing interactions between spin, orbital, and charge degrees of freedom and lattice distortions on physical properties.[1–5] While a coherent understanding of the origin of CMR in the manganates is yet to emerge, it is clear that the lattice distortions [due to the size of the A-site cations and Jahn-Teller distortion of the B-site Mn(III) cations] together with the mixed valency of the B-site Mn(III/IV) cations are essential.[1,4–6] The latter can be achieved by partially replacing the trivalent lanthanide ion with a divalent ion such as Sr or Ca or by the introduction of defects in the structure.

A number of manganates exhibit unusual lattice deformations at low temperatures that reflect the magnetic order.[7] An increase in the cell volumes when going from a ferromagnetic-insulator (FMI) to a ferromagentic-metal (FMM) has been previously reported in a number of manganates including $La_{0.83}Sr_{0.17}MnO_3$ and $Pr_{0.7}Ca_{0.3}MnO_3$.[8,9] In both cases a change in electronic properties is associated with the structural phase transition and delocalization of the charge carriers altering the unit-cell volume. In $Pr_{0.7}Ca_{0.3}MnO_3$ the smaller FMI structure is in the orthorhombic space group *Imma* whereas the larger FMM state is tetragonal in $I4/mcm$. Nojiri and co-workers[10] suggested that the driving force of the FMM to FMI transition is the cooperative ordering of spins and orbitals but not charges. This raises the possibility of observing a similar expansion in the unit-cell volume at the Neel temperature in trivalent manganates where the Jahn-Teller effect results in orbital ordering but no charge ordering occurs.

In the present work we report the existence of an unusual negative thermal expansion (NTE) in the trivalent Mn perovskite MnF_3. The transition from thermal contraction to expansion coincides with the Neel temperature demonstrating

this to be an unusual example of magnetostriction in a trivalent Mn perovskite. This behavior is reminiscent to that seen in Invar alloys, so named because of their invariable volume when heated.[11] That is there is a magnetic transition to a higher volume state in the absence of a crystallographic phase transition. The magnetic structure of MnF_3 is not inconsistent with the commonly accepted model for the Invar effect.[12]

A commercially available sample of MnF_3 was used in this work. Powder neutron diffraction (PND) data between 300 and 5 K were collected on the HRPD at ANSTO's HI-FAR reactor using 1.88 Å neutrons.[13] Synchrotron diffraction patterns between 10 and 500 K were recorded on Beamline X7A at the NSLS at Brookhaven National Laboratory.[14]

That MnF_3 has a monoclinic structure at room temperature, as first described by Hepworth and Jack[15] was rapidly confirmed in both the synchrotron and neutron-diffraction studies. The room-temperature structure was refined from the powder-neutron-diffraction data in space group $C2/c$. The average Mn-F distances for the two independent Mn sites within this monoclinic cell are approximately equal. However, while the local geometry of the two sites are quite different, both can be described as having three different Mn-F distances, two long ≈ 2.05, two short ≈ 1.80, and two intermediate $\approx 1.85–1.92$ Å. The monoclinic structure is a consequence of independent in-phase or -tilts around both the [100] and [011] axes ($a^-b^-b^-$). These tilts, in turn, are influenced by the large Jahn-Teller effect of the d^4Mn^{III} ion, so that two of the Mn-F distances are noticeably longer. In the case of TiF_3 which has a rhombohedral structure in space group $R\bar{3}c(a^-a^-a^-)$ the tilting of the TiF_6 octahedra results in a noticeably smaller distortion of the octahedra.[16,17]

Cooling MnF_3 results in a contraction in the lattice parameters and unit-cell volume, Fig. 1. Near 45 K a shallow minimum in the various lattice parameters and the cell volume is observed, after which these increase rapidly as the temperature is further lowered, Fig. 2. The temperature at
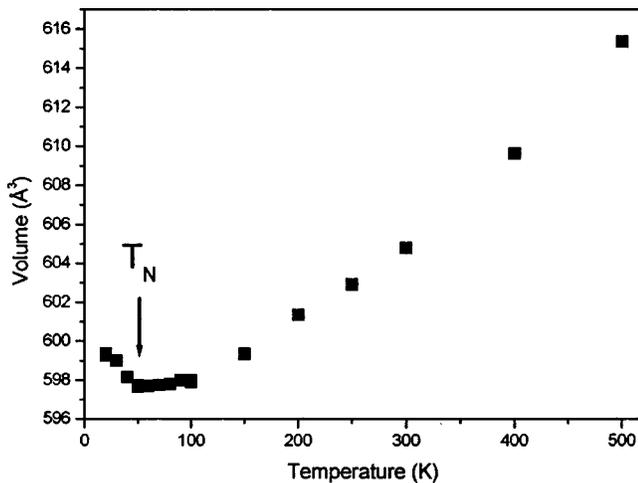
FIG. 1. Temperature dependence of the unit-cell volume of MnF_3. The Neel point is shown.

which the minimum in volume is observed is in good agreement with the Neel temperature measured using a superconducting quantum interference device magnetometer, $T_N \approx 43$ K.[18] The evolution of the magnetic structure of MnF_3 determined from the PND measurements indicates that the low-temperature NTE is related to the change in magnetic properties of MnF_3. There is no evidence from the synchrotron x-ray or neutron-diffraction study for a structural phase transition at T_N, the structure remains in the $C2/c$ space group down to 5 K. In this respect the observed magnetostriction is noticeably different than that observed in most manganates where it is accompanied by a structural phase transition [8,9]. Nanocrystalline and polycrystalline chromium shows a similar onset of NTE around 240 K as a result of a magnetic phase transition.[19,20] The NTE observed here is different from that seen in classical NTE oxides such as quartz[21] and ZrW_2O_8 (Ref. 22) in that the NTE in these materials is not associated with a magnetic transition.

Heating the sample to 500 K results in some decomposition of the sample and the formation of MnF_2 and Mn_2F_5 as was also noted by Rau and co-workers.[23] Unlike the case of $LaMnO_3$[24,25] where heating results in an increase in symmetry due to a combination of the quenching of the Jahn-Teller effect and the reduction of the MnO_6 tilts, the distortion and tilt angles of the MnF_6 octahedra remain essentially constant up to these temperatures. Orbital ordering clearly persists in MnF_3 over the entire temperature range studied.

The NTE observed in MnF_3 is highly anisotropic with the low-temperature expansion occurring mainly within the crystallographic ab plane. Both the absolute and relative expansion along the long crystallographic c axis is noticeably smaller, although it is still detectable. In order to understand this anisotropy we have reexamined the magnetic structure of MnF_3.

The magnetic structure of MnF_3 was first determined by Wollan and co-workers[26] and in agreement with this previous work we find MnF_3 has an A-type antiferromagnetic structure as is also observed in $LaMnO_3$.[24,27] Neglecting the distortions of the MnF_6 octahedra the structure can be
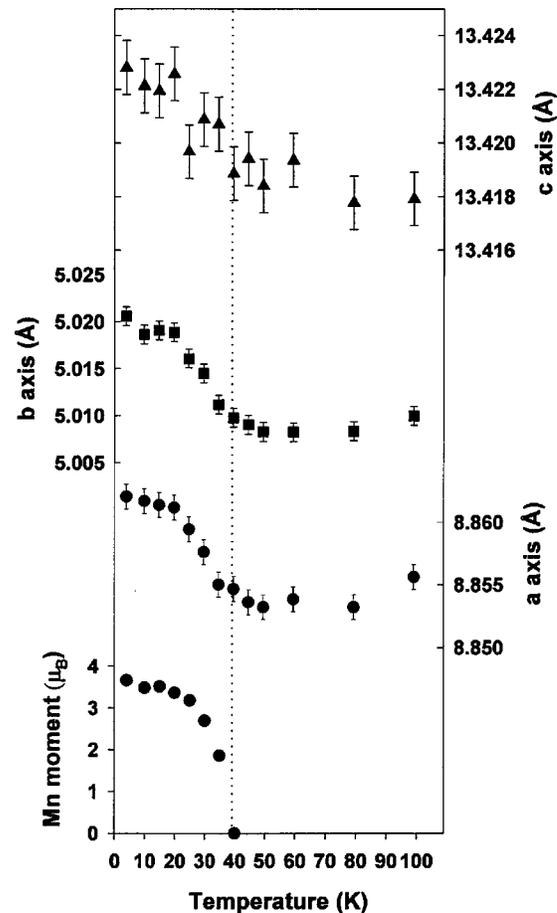
FIG. 2. Temperature dependence of the refined lattice parameters and Mn magnetic moments for MnF_3. The magnetic moments of the two independent Mn atoms have been constrained to be equal.

represented as a tetragonal A-type antiferromagnet as illustrated in Fig. 3. The orbital ordering allows for the singly occupied d_{z^2} orbital to interact with an unoccupied $d_{x^2-y^2}$-type orbital via the fluorine p orbitals. This results in alternating long-short Mn-F distances within the ferromagnetic layers and an intermediate Mn-F distance separates the layers. The spins in the alternate layers aligned approximately along the c-axis are coupled in an antiferromagnetic manner. The tilting of the MnF_6 octahedra results in a displacement of the F atoms away from the Mn-Mn vectors and perturbs the superexchange overlap. To a good approximation the $d_{x^2-y^2}$ and d_{z^2} orbitals are aligned out of phase in the ab plane and they are in phase along the c axis.

The spins within the ferromagnetic layers align collinear at the Neel temperature resulting in the expansion of these layers. At the same temperature an antiferromagnetic coupling of the spins between layers occurs, however this does not induce the same degree of expansion in the unit-cell. We would expect that the individual Mn-F distances should vary systematically at the Neel temperature, that this could not be observed is presumably a result of the limited d range of neutron-diffraction data.

(a)

(b)
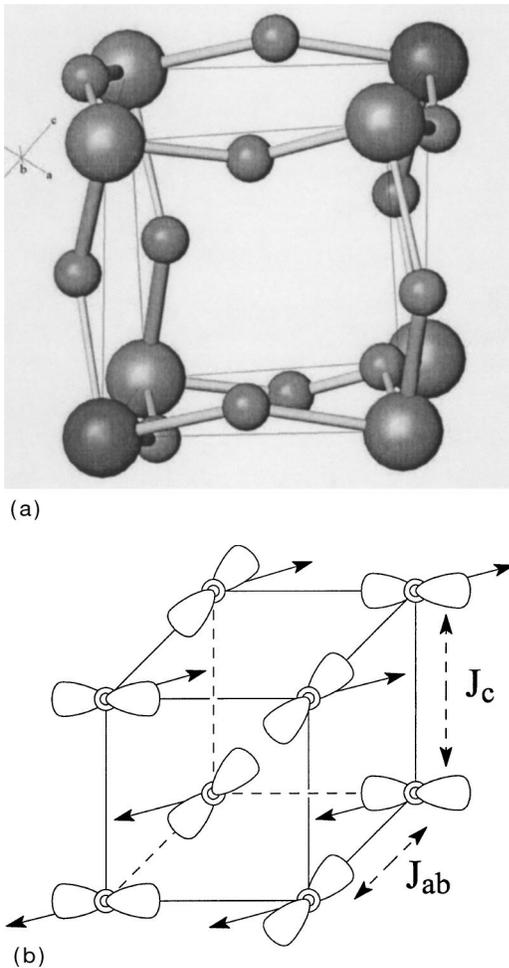
FIG. 3. (a) (Color online) Representation of the structure of MnF_3. The Mn atoms are shown as the large spheres. The three different types of Mn-F distances are represented by bonds of differing thickness. The longest Mn-F distances (narrow lines) are orientated parallel to the shortest Mn-F bonds (thick lines). The displacement of the F ions from the edges of the Mn cube is apparent. The antiferromagnetic layers run vertically in this representation. 3(b) Idealized magnetic structure for MnF_3.

The behavior of the cell volume below ≈ 45 K is reminiscent of the Invar effect observed in magnetic alloys such as $Fe_{65}Ni_{35}$.[28] In such alloys the temperature independence of the cell volume is a consequence of the normal thermal contraction, resulting from a reduction in the magnitude of the lattice vibrations on cooling, being off set by a transition from the low volume paramagnetic state to a high volume ferromagnetic state. On cooling polarization of the spins is induced by their alignment, which increases the kinetic energy of the $3d$ electrons. Increasing the volume reduces the kinetic energy of the system by increasing the density of states in the $3d$ bands. The Invar effect is very rare in materials other than alloys.[29,30] Kiyama *et al.* have presented evidence for the Invar effect in the $4d$ ferromagent $SrRuO_3$.[29] These workers observed a small increase along the c axis in $SrRuO_3$ below the Curie temperature, which corresponds to the magnetic easy axis, and suggest the Invar effect is responsible for a $\approx 0.1\%$ expansion of the unit-cell volume. The $\approx 0.3\%$ expansion of the unit-cell volume observed here in MnF_3 is around three times that calculated for $SrRuO_3$ and is comparable to that displayed in classic Invar alloys such as $Fe_{65}Ni_{35}$.

The magnetostriction in MnF_3 resembles the 2γ-state model initially developed by Weiss to explain the Invar effect [12]. Weiss proposed that Invar alloys have two different magnetically ordered states, a large volume ferromagnetic ground state and energetically near by a low volume antiferromagnetic state. As the temperature increases the AF state becomes thermally populated and the smaller volume of this state compensates for the vibrational thermal expansion. Just above T_N this state is effectively fully populated so the normal thermal expansion is observed. Schilfgaarde and co-workers have recently presented *ab initio* calculations of the volume dependencies of the magnetic and thermodynamic properties in the classic Invar Fe-Ni alloys, and advanced and improved on the classical Weiss model.[31,12] Recently a large negative magnetic contribution to the thermal expansion in Fe-Pt Invar alloys was identified by first-principle calculations.[32]

Very recently Okamoto, Ishihara, and Maekawa[33] demonstrated that the elastic coupling constants for $LaMnO_3$ show a characteristic change at the Neel temperature as a result of electron-electron (spin-spin) and electron-lattice (spin-phonon) interactions. While these authors have not discussed such interactions in terms of the Invar effect their conclusions can be rationalized by such an effect. It is possible that a similar mechanism is active in MnF_3 and is responsible for the peculiar magnetostriction observed here. First-principle calculations would be of great value to understand this unusual low-temperature behavior.

In summary we have observed an unusual NTE in the simple Mn(III) perovskite MnF_3. The unusual expansion of the unit-cell volume of MnF_3 at low temperatures suggests this to be a consequence of the magnetic ordering. Although magnetostriction has been observed in mixed valent Mn(III/IV) perovskites the current example is unique in that only Mn(III) is present. Since the orbital ordering persists over the entire temperature range (5–500 K) the observed magnetostriction is a consequence of spin ordering in the absence of charge ordering. That spin ordering alone can result in an unusual thermal expansion in cell volumes is very well known for Invar alloys, however it is very rare in compounds such as metal oxides or fluorides. This opens up the possibility of observing similar effects in a new class of magnetic materials based on the ubiquitous perovskite structure.

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