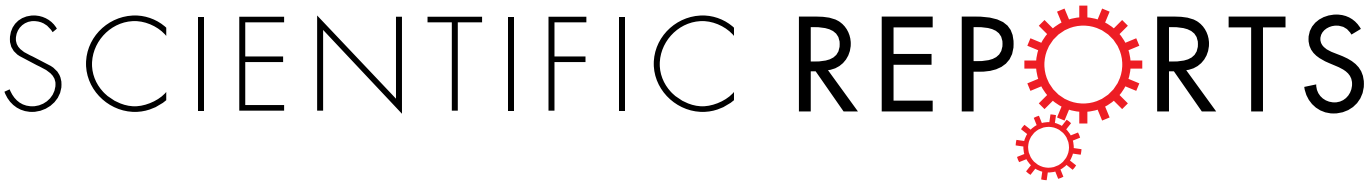

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# Uniaxial ferroelectric quantum criticality in multiferroic hexaferrites $BaFe_{12}O_{19}$ and $SrFe_{12}O_{19}$

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**$BaFe_{12}O_{19}$ is a popular M-type hexaferrite with a Néel temperature of 720 K and is of enormous commercial value ($3 billion/year). It is an incipient ferroelectric with an expected ferroelectric phase transition extrapolated to lie at 6 K but suppressed due to quantum fluctuations. The theory of quantum criticality for such uniaxial ferroelectrics predicts that the temperature dependence of the electric susceptibility $\chi$ diverges as $1/T^3$, in contrast to the $1/T^2$ dependence found in pseudo-cubic materials such as $SrTiO_3$ or $KTaO_3$. In this paper we present evidence of the susceptibility varying as $1/T^3$, i.e. with a critical exponent $\gamma = 3$. In general $\gamma = (d + z - 2)/z$, where the dynamical exponent for a ferroelectric $z = 1$ and the dimension is increased by 1 from $d_{eff} = 3 + z$ to $d_{eff} = 4 + z$ due to the effect of long-range dipole interactions in uniaxial as opposed to multiaxial ferroelectrics. The electric susceptibility of the incipient ferroelectric $SrFe_{12}O_{19}$, which is slightly further from the quantum phase transition is also found to vary as $1/T^3$.**

Hexagonal ferrites are the most common magnetic materials with 90% of the $4 billion world market. 300,000 tons of hexagonal $BaFe_{12}O_{19}$ are produced every year, which corresponds to 50 grams for every person on Earth[1,2]. Primary uses are magnetic credit cards, bar codes, and small motors, as well as low-loss cheap microwave devices. In 2011 Fujifilm produced a barium hexaferrite-based tape with a memory of five terabytes – the equivalent of eight million books. At present this material has a new aspect of fundamental interest – it is nearly ferroelectric as the temperature approaches absolute zero. Incipient ferroelectrics at low temperature, i.e. materials close to a ferroelectric quantum phase transition, are expected to be important for a wide range of advanced material applications including for example, electro-caloric refrigeration, quantum memory devices, and cryogenic electronic switches, as their properties can be readily controlled by voltage gates and strains.

Very recently we examined[3] the quantum criticality of uniaxial ferroelectric tris-sarcosine calcium chloride-bromide (TSCC:Br) and found that the low-temperature dielectric constant diverged with temperature as $1/T^2$, as in pseudo-cubic compounds such as strontium titanate[4] and in contrast to the inverse cubic dependence first predicted by Khmelnitskii and Shneerson[5], and were able to show that this paradox arises from the ultra-weak ferroelectric dipoles in that material. Here we report the study of a second uniaxial paraelectric, M-type barium hexaferrite, near its ferroelectric quantum phase transition, which is a strongly displacive system, with an $A_{2u}$ symmetry soft mode frequency decreasing at the zone centre to 42 $cm^{-1}$ as $T$ goes to zero[6]. The only other low-$T$ multiferroic studied in detail previously is $EuTiO_3$[7] which appears to be slightly too far from the critical point to manifest quantum critical behaviour.

There has been some controversy concerning ferroelectricity in this family of M-type hexaferrites: polarization-electric field hysteresis loops $P(E)$ of $SrFe_{12}O_{19}$ at 300 K were published by Tan and Wang[8,9], and there is also a recent theoretical paper[10] by Wang and Xiang that predicts a paraelectric to antiferroelectric phase

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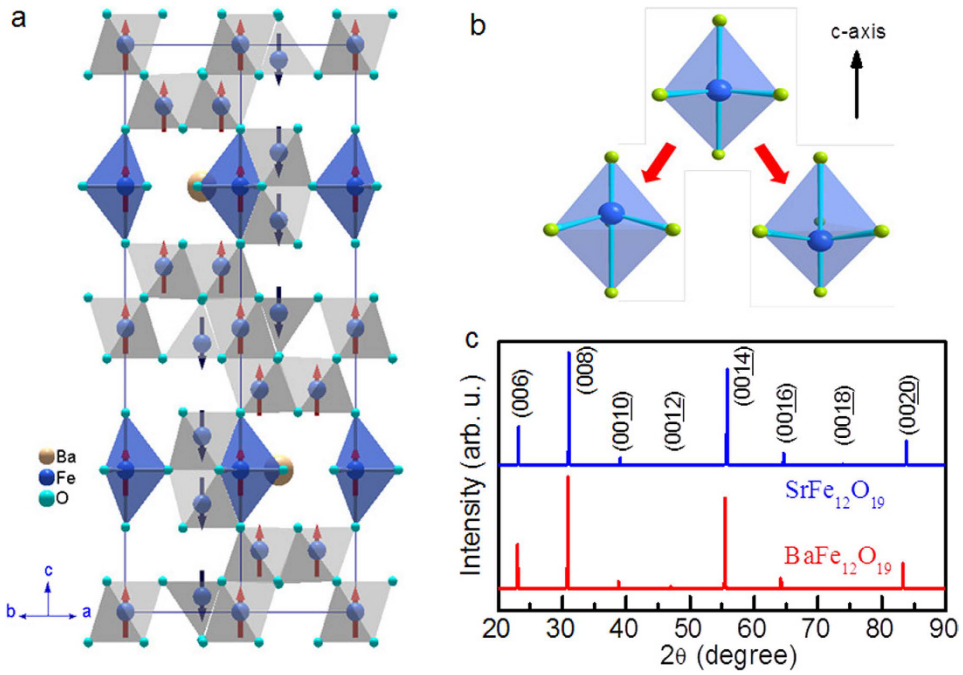


**Figure 1. Crystal and multiferroic structures of M-type hexaferrites.** (**a**) The crystal and magnetic structures of M-type Ba- and Sr- hexaferrites. The arrows represent the magnetic moments of $Fe^{3+}$ ions. (**b**) The off-equator displacements of $Fe^{3+}$ in the $FeO_5$ bypyramidal sites induce uniaxial electric dipoles along *c* axis. Quantum fluctuations between two 4e sites prevent the onset of long-range ferroelectric ordering down to the lowest temperature. (**c**) The single-crystal x-ray diffraction patterns at room temperature of prepared $BaFe_{12}O_{19}$ and $SrFe_{12}O_{19}$ crystals.

transition for $BaFe_{12}O_{19}$ at about 3.0 K. In this context it is important to note that $SrFe_{12}O_{19}$ and $(Ba,Sr)Fe_{12}O_{19}$ are n-type semiconductors[11] with bandgaps at approximately $E_g = 0.63$ eV and rather heavy electrons and holes: m(light e) = 5.4 $m_e$; m(heavy e) = 15.9 $m_e$; m(light h) = 10.2 $m_e$; m(heavy h) = 36.2 $m_e$ and highly anisotropic conductivity, so it is important to discriminate between true ferroelectric hysteresis and leakage current artefacts. For electric fields applied normal to the c-axis, the electrical conductivity is ca. 50× greater than along c, which will create strong leakage currents. The present work and ref. 12 show that these suggested ferroelectric transitions do not occur at finite temperatures and that $BaFe_{12}O_{19}$ retains its paraelectric $P6_3/mmc$ symmetry ($D_{6h}$) down to zero temperature. When fitting the inverse susceptibility $1/\chi_E$ to a Curie-Weiss law at higher temperatures (the linear part of the curve), an extrapolation to $1/\chi_E = 0$ gives an expected Curie temperature, like that in $SrTiO_3$ or $KTaO_3$, at ca. 6 K (similar to the 35 K value in $SrTiO_3$). However the anticipated ferroelectric state does not stabilize and is suppressed by quantum fluctuations (analogous to the freezing temperature of liquid helium) resulting in a paraelectric ground state with quantum critical fluctuations. The proximity to the quantum critical point is evident from a rapidly rising dielectric susceptibility as the temperature is lowered and a soft $A_{2u}$-symmetry $q = 0$ long wavelength phonon mode with a frequency that decreases to 42 $cm^{-1}$ as *T* approaches zero[6]; we designate this frequency gap (minimum in the transverse-optical phonon frequency in the low temperature limit at $q = 0$) as Δ. A good review of work on $SrFe_{12}O_{19}$ was given this year by Hilczer *et al.*[13]. From a magnetic point of view Ba-hexaferrite is unusual in that although all 24 spins per primitive unit cell (two formula groups) are $Fe^{+3}$, it is a ferrimagnet with 8 spins up (at tetrahedral, octahedral, and five-fold coordinated sites) and 16 down (all at octahedral sites), as shown in Fig. 1a. This produces a strong ferromagnetic moment, unlike weak canted antiferromagnets (it is often termed a Lieb-Mattis ferrimagnet[14]).

M-type hexaferrite single crystals were prepared by the flux method. The single-crystal x-ray diffraction (XRD) patterns at room temperature shown in Fig. 1c suggest that our samples are single-phase M-type with $c = 23.18$ Å for $BaFe_{12}O_{19}$ and 23.04 Å for $SrFe_{12}O_{19}$, respectively, agreeing with the original 1959 single-crystal value of Brixner[15,16]. The structure is not completely agreed upon in the literature: Ganapathi *et al.*[17] report a tripled unit cell along the a-axis for flux-grown crystals like those in the present work; this differs from the original structural determination[15] with $a = 5.895$ Å. However, this is unimportant for the present study since the ferroelectric properties are thought to involve only symmetry changes along the c-axis.

In a previously published paper[12] we found that M-type ferrimagnetic hexaferrites $(Ba,Sr)Fe_{12}O_{19}$ are a new family of magnetic quantum paraelectrics along the *c*-axis only. This preservation of c-axis six-fold symmetry is compatible with the $A_{2u}$-symmetry soft mode reported from the Rostov group, which retains the hexagonal symmetry. The resulting symmetry of the crystal, were it to undergo a transition into a ferroelectric phase, is therefore probably $C_{6v}$ point group symmetry and $P6_3/mc$ space group. Because there is no change in hexagonal crystal class, this transition would be purely ferroelectric and not ferroelastic[18], with no hysteresis in its stress-strain

relationship. That may be important with regard to descriptions of the system close to quantum criticality, implying that no elastic order parameter is a conjugate force.

As shown in Fig. 1b, M-type hexaferrite exhibits a new mechanism for local electric dipoles based on the magnetic $Fe^{3+}$ ($3d^5$) ion, violating the $d^0$ rule of Nicola Hill[19]. The competition between the long-range Coulomb interaction and short-range Pauli repulsion in a $FeO_5$ bipyramid with proper lattice parameters would favour an off-centre displacement of $Fe^{3+}$ that induces a local electric dipole. Such local dipoles cannot order down to the lowest temperatures in the specimens we measured but ferroelectric ground states may be reached perhaps via tuning with strains, chemical substitution or by varying the lattice density.

## Results and Discussion

Our low temperature inverse electric susceptibility data $1/\chi_E$, (related to the measured dielectric constant $\varepsilon$ by $\chi_E = \varepsilon - 1$), are shown in Fig. 2. The measurements were obtained with a pumped helium-3 cryostat for both cooling and heating cycles, typically at rates of 10 mK/minute (overnight runs). Here we see that below approximately 6 K in $BaFe_{12}O_{19}$ and 20 K in $SrFe_{12}O_{19}$ there is a non-monotonic dependence; we have previously reported such effects in $SrTiO_3$, $KTaO_3$[4], and tris-sarcosine calcium chloride (TSCC)[3] and shown quantitatively without adjustable parameters in the former cases that they arise from acoustic phonon coupling (electrostriction). Similarly such behaviour may occur from coupling of the polarization order-parameter field with any other auxiliary filed such as the magnetisation (magneto-capacitance or indirectly via magneto-striction). In $SrTiO_3$ and $KTaO_3$ the upturn in the inverse susceptibly, as determined by measurements and theory without adjustable parameters, occur when $T$ is less than 10% of $T_x$ where $T_x$ is the temperature scale associated with the soft transverse-optical phonon frequency at the zone centre, $\Delta$, in the zero temperature limit, i.e. $T_x = \hbar\Delta/k_B$. This means that we can attempt to fit the dielectric susceptibility data only for $T > 0.1T_x$ to a quantum criticality model in the absence of magneto-electric or electrostrictive coupling terms, the parameters for which are not currently available for our samples. $0.1T_x = 6$ K for $BaFe_{12}O_{19}$ as determined from measurements[6], and estimated to be 20 K in $SrFe_{12}O_{19}$ which is further away from the quantum phase transition. Note that precisely at a ferroelectric quantum critical point, the frequency gap $\Delta$ vanishes and both $T_x$ and the Curie temperature $T_C$ are exactly zero. This means that such upturns only exist in samples with paraelectric ground states some distance away, but close to, the quantum phase transition. Another cross-over temperature exists for the upper temperature limit for any power-law exponent: In measurements and theory in $SrTiO_3$ and $KTaO_3$ we found that a single quantum critical exponent extends up to ca. 10% of the characteristic temperature $T^*$. $T^*$ is analogous to the Debye temperature but of the soft (critical) transverse-optical phonon mode and is given by $T^* = \hbar\nu Q/k_B$ where $\nu$ is the gradient of the frequency with respect to wave-vector $q$ at low temperatures from a dispersion of the form $\Omega^2 = \Delta^2 + \nu^2 q^2 + \ldots$ in the limit that $\Delta$ goes to zero, and $Q$ is the value of $q$ at the Brillouin zone boundary. It can also be estimated from $k_B T^* = \hbar\Omega(q = Q)$ where $\Omega(q = Q)$ is the measured value of the transverse-optic mode frequency in the low temperature limit at the Brillouin zone boundary, $q = Q$. The soft mode dispersion in $BaFe_{12}O_{19}$ has not been measured, but based upon its frequency at $q = 0$ and the heavy masses in $BaFe_{12}O_{19}$, we estimate $T^*$ to be approximately 150 K. Therefore in Fig. 2c we fit the measured dielectric susceptibility $\chi_E(T)$ over the range 6–15 K for $BaFe_{12}O_{19}$, i.e. between the lower and upper crossover temperatures $0.1T_x$ and $0.1T^*$ respectively. Figure 2c shows that $1/\chi_E$ varies as $T^3$ for several thousand data points in the region, thus supporting the theory of Khmelnitskii and Shneerson[5] of quantum criticality for a uniaxial ferroelectric. Above 10% of $T^*$ one expects the system to exhibit classical Curie-Weiss behaviour as observed in our data in Fig. 2a,b. We emphasize that the critical exponent is measured with unusual precision as $\gamma = 3.0 +/- 0.1$ – and certainly not close to $\gamma = 2.0$ for multiaxial quantum critical systems as highlighted in the lower insets in Fig. 2c,d – over thousands of data points – every 5 mK in the range). Conversely, none of the other systems we have studied in the past gave exponents near 3.0 over any temperature range[3,4]. High pressure work by which $T_c$ may be brought up through $T = 0$ will be the subject of future work, but the results of dielectric measurements in the presence of "chemical pressure" obtained by replacing Ba-ions with smaller Sr-ions is shown in Fig. 2b,d, where a cubic temperature dependence agrees with the measured data in the range 20 K to 35 K for $SrFe_{12}O_{19}$.

Hexaferrites are important and well known magnetic materials. Our work shows that at cryogenic temperatures the magnetic phase coexists with a quantum fluctuating electrical dipole phase coupled to the magnetic system. The quantum critical phase is evident by the fact that the equilibrium thermodynamic quantities such as the susceptibility, depend on both the static and dynamic (frequency-dependent) properties of the system, which results in a unity rise in the effective dimension. In the uniaxial materials investigated here, the cryogenic phase is particularly novel since apart from short-range interactions, long-range anisotropic electrical dipole interactions provide a further unity increase in the effective dimension to $d_{\text{eff}} = 5$ as detected by our high-precision dielectric measurements. The magnetic ordering temperature and magneto-electric behaviour of these materials may be tuned by chemical substitution realising a magnetic quantum phase transition and quantum glassy or relaxor type phenomena in different parts of the phase diagram. A detailed study of the frequency dependence of the dielectric and magnetic properties in these chemically or pressure tuned hexaferrites is likely to be the subject of promising future work.

## Methods

M-type hexaferrite single crystals were prepared by the flux method. The raw powders of $BaCO_3$ ($SrCO_3$), $Fe_2O_3$, and fluxing agent $Na_2CO_3$ were weighed in the molar ratio 10.53% : 26.3% : 63.17% and were well mixed. The mixed raw powder was put in a Pt crucible and heated to 1250 °C for 24 h in air, then cooled down to 1100 °C at a rate of 3 °C/min and finally quenched to room temperature. The samples (ca. 2 mm on a side) were characterized by single-crystal x-ray diffraction at room temperature by using a Rigaku X-ray diffractometer.

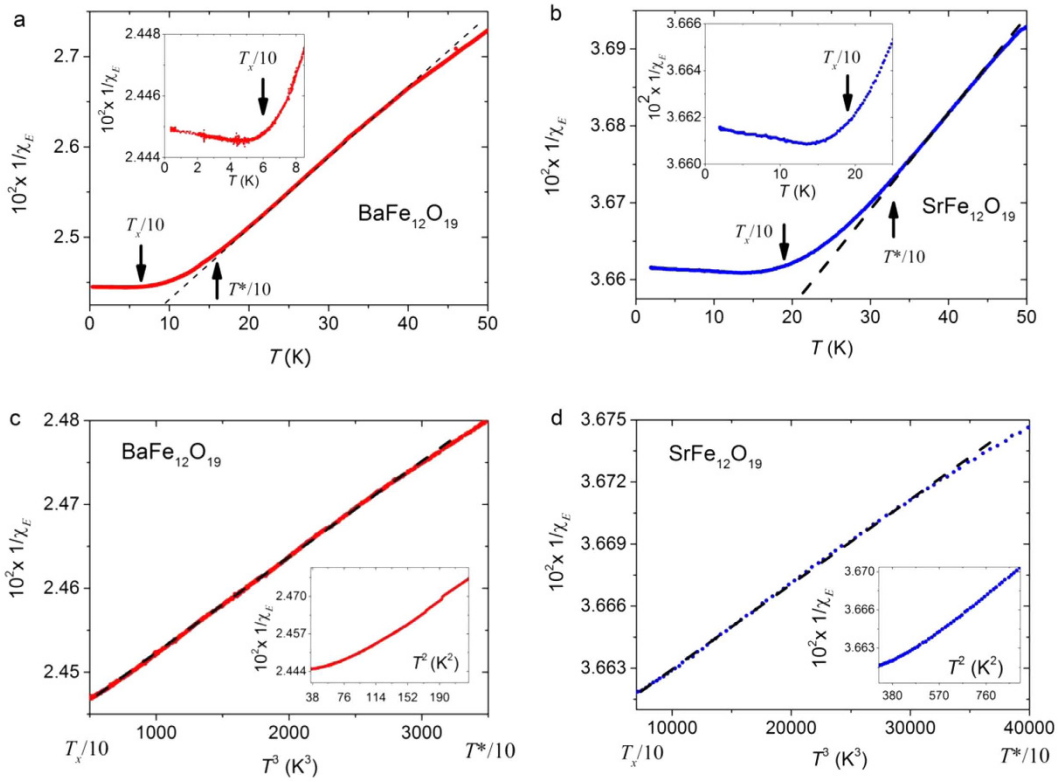


**Figure 2. Dielectric susceptibility measurements along the c-axis in Ba and Sr M-type hexaferrites.** The main figures in (**a**,**b**) show the temperature depence of the inverse electric susceptibility $1/\chi_E$ for $BaFe_{12}O_{19}$ and $SrFe_{12}O_{19}$ respectively. The classical Curie-Weiss like behaviour (linear part of the curve) at higher temperaures crosses over to a different form below the characteristic temperature scale $T^*/10$ due to the proximity of a ferroelectric quantum phase transition. The insets in (**a**,**b**) show a magnification of the low temperature region of $1/\chi_E$ against temperature in which anomolous upturns are observed below the temperature scale $T_x/10$. In (**c**,**d**) the inverse electric susceptibily is plotted against $T^3$ over the range of temperatures between the anomolous upturn at low $T$ and the classical Curie-Weiss regime at high $T$, i.e. between $T_x/10$ and $T^*/10$ as explained in the text. This is between 6 K and 15 K for $BaFe_{12}O_{19}$ in (**c**) and between 20 K and 35 K for $SrFe_{12}O_{19}$ in (**d**). The dashed straight lines are guides to the eye. The lower insets in (**c**,**d**) confirm that no $T^2$ dependence of $1/\chi_E$ fits the data which would be expected for a multi-axial as opposed to a uniaxial ferroelectric quantum critical system. Recent attempts[20] by others to fit data over a wide temperature range to a single exponent are in our opinion not reliable tests.

The dielectric measurements were carried out in a pumped helium-3 cryostat at temperatures as low as 0.3 K. Silver paste was painted on the surfaces (ab plane) of a thin plate of each crystal and an Andeen-Hagerling or Agilent 4980 A LCR meter was used to measure the dielectric susceptibility at frequencies typically in the range 1 kHz to 100 kHz.

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## Author Contributions

The project was designed by S.E.R., J.F.S. and Y.S. Samples were grown by Y.-S.C., S.-P.S. and B.E.W. Data were taken by S.E.R., Y.-S.C., S.-P.S. and A.T.J. The manuscript was written by S.E.R., J.F.S. and Y.S.

## Additional Information

**Competing financial interests:** The authors declare no competing financial interests.

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