Letter

Thermal magnetic fluctuations of a ferroelectric quantum critical point

Alexander Khaetskii1,∗, Vladimir Juričić2 and Alexander V Balatsky1,2

1 Department of Physics, University of Connecticut, Storrs, CT 06269, United States of America
2 Nordita, KTH Royal Institute of Technology and Stockholm University, Roslagstullsbacken 23, SE-106 91 Stockholm, Sweden

E-mail: alexander.khaetskii@uconn.edu

Received 3 July 2020, revised 11 September 2020
Accepted for publication 23 September 2020
Published 28 October 2020

Abstract

Entanglement of two different quantum orders is of interest of the modern condensed matter physics. One of the examples is the dynamical multiferroicity, where fluctuations of electric dipoles lead to magnetization. We investigate this effect at finite temperature and demonstrate an elevated magnetic response of a ferroelectric near the ferroelectric quantum critical point (FE QCP). We calculate the magnetic susceptibility of a bulk sample on the paraelectric side of the FE QCP at finite temperature and find enhanced magnetic susceptibility near the FE QCP. We propose quantum paraelectric strontium titanate as a candidate material to search for dynamic multiferroicity. We estimate the magnitude of the magnetic susceptibility for this material and find that it is detectable experimentally.

Keywords: magnetic susceptibility, dynamical multiferroicity, quantum critical point

Supplementary material for this article is available online

(Some figures may appear in colour only in the online journal)

Materials that can undergo phase transitions, especially those exhibiting an interplay of two or more quantum orders attract special interest. One of the examples featuring an entanglement of two different quantum orders is the dynamic multiferroicity (DMF), the concept reflecting the connection between electric and magnetic properties [1–4].

Ferroelectric quantum critical points (FE QCPs) are an important part in the discussion of FE behaviour, particularly in displacive quantum paraelectrics (PE) [5–7]. The plethora of effects that occur near an FE QCP have been investigated in various contexts [5–15]. In the DMF phenomenon magnetization $\mathbf{M}$ (i.e. magnetic moment per unit volume) is induced by time-dependent oscillations of electrical polarization $\mathbf{P}$ (an electric dipole moment per unit volume):

$$
\mathbf{M} = \lambda \mathbf{P} \times \frac{\partial \mathbf{P}}{\partial t} \quad \lambda \approx \frac{a_0^3}{\epsilon c} \frac{(m_+ - m_-)}{(m_+ + m_-)}.
$$

Here $a_0$ is the lattice spacing, and $c$ is the speed of light. The form of magnetization in the above equation is a consequence of the relation between the magnetic moment and the angular momentum for a rotating electric dipole, see also equation (4) and the discussion therein. An expression for the coupling constant $\lambda$ is obtained (equation (4)) for the model of optical long wave oscillations in the material with one cation and one anyon per unit cell, with charges $\pm e_+$ and masses $m_{\pm}$. One can induce DMF by applying external drive-like light field to ferroelectrics. An alternative approach is to rely on inherent fluctuations present in the material near phase transition.

* Author to whom any correspondence should be addressed.

Original content from this work may be used under the terms of the Creative Commons Attribution 4.0 licence. Any further distribution of this work must maintain attribution to the author(s) and the title of the work, journal citation and DOI.

© 2020 The Author(s). Published by IOP Publishing Ltd Printed in the UK
In this work we consider a bulk material in the vicinity of a ferroelectric phase transition, and investigate the enhanced magnetic susceptibility at finite temperatures upon approaching the QCP. The main result of our work is the elevated magnetic susceptibility at finite temperature using the Kubo formula and the renormalization-group sense than the leading one proportional to the velocity, and as such can be neglected.

For the (static) magnetic susceptibility in the high-$T$ limit, at $T > h\omega_0(T, \delta)$, based on simple physical arguments (see below), supported by a formal analysis [see equation (14)], we find

$$\chi(\omega = 0, T, \delta) \approx \left( e, \hbar \right)^2 \frac{T^2}{\hbar^2 s_\perp^2(\delta)}$$

Here $M_0 = m_+ m_- / (m_+ + m_-)$, we have assumed that $(m_+ - m_-) / (m_+ + m_-) \simeq 1$, and set $\hbar^2 = 1$ hereafter. Thus, a strong increase of the magnetic susceptibility may occur while approaching the QCP: the underlying reason for this enhancement is an increase of the density of states of phonons due to the softening of the ferroelectric mode near the QCP, which is consistent with $z > 1$.

We now provide the estimate of the magnetic susceptibility as given in equation (3) using rather simple physical arguments. In our case, although the system is an insulator, we use the Pauli susceptibility because the *fluctuating* electric dipoles, according to our mechanism, yield the magnetic response. We start with the well known expression for the static Pauli susceptibility $\chi \approx \mu_0^2 \rho(\varepsilon)$, where $\mu_0$ is the Bohr magneton and $\rho(\varepsilon)$ is the density of states of the excitations at a corresponding energy. Then one needs to replace the Bohr magneton with the nuclear magneton $\mu_0$ (determined by the reduced mass of two atoms in a cell). Since phonon excitations yield the fluctuating dipoles which in turn give rise to the magnetization [see equation (1)], we calculate the density of states of phonons at a given temperature $T$, using the spectrum given by equation (2). At $T > h\omega_0$ the phonon density of states is $\rho(\varepsilon) \approx q^3 T / \hbar \omega_\perp(qT) \simeq (1/\hbar s_\perp)(T/\hbar s_\perp)^2$, where $\hbar s_\perp = T/\hbar s_\perp$ is the thermal momentum of a phonon, yielding equation (3). The estimate in equation (3) corresponds to the result obtained below more formally within the Kubo formalism, see equations (13) and (14). The case $T \ll h\omega_0$ can be treated in a similar manner [24].

As mentioned before, one can reach the vicinity of the critical value $\delta_c = 1$ by applying strain or by O$^{18}$ isotope substitution. For example, for the value of 95% of isotope concentration, an approach to a critical point by changing temperature in a relatively narrow interval around $T_c \approx 25$ K was achieved [21]. Moreover, the temperature dependence of the squared frequency of the ferroelectric mode near $T_c$ obeyed the Curie–Weiss law. This might imply a suppression of the quantum fluctuations and our results obtained with the use of the bare Greens’s functions of optical phonons can be applied in the close proximity of the critical point.

To gain further insight into the role of the fluctuating dipoles associated with the soft phon modes, it is instructive to derive an expression for the parameter $\lambda$ in equation (1), which relates magnetization and electric polarization, by taking into account its microscopic origin. This analysis is based on the well-known relation between the magnetic moment $\mu$ and the orbital angular momentum $L$, for a point-like particle with electric charge $e$ and mass $m$. Considering the optical long wave oscillations in a system with two atoms per unit cell, we use $m_+ u_+ + m_- u_- = 0$. Here $u_+$ and $u_-$...
are the displacements of positive and negative ions. Introducing relative displacement vector $u = u_+ - u_-$, we obtain for the orbital angular momentum of the unit lattice cell, $L = (m_+m_- / (m_+ + m_-)) [u \times \dot{u}]$, where $\dot{u} \equiv \partial u / \partial t$. For the magnetic moment of the unit cell $m = (e_+ / 2e)(\sum_{i=\pm} \zeta u_i \times \dot{u_i})$, we obtain

$$m = \frac{e_+ (m_+ - m_-)}{2e (m_+ + m_-)} [u \times \dot{u}] = \frac{e_+ (m_+ - m_-)}{2m_+ + m_-} L,$$  

(4)

where $e_+$ is the effective charge of the cation. The expression for the coupling constant $\lambda$ directly follows from equation (4), if one takes into account that $m_0^2 M = a_0^2 [M]$ and $P = e_+ u / a_0^2$.

Magnetic susceptibility: finite temperature case. We now derive our main results [including equation (3)] using the Kubo formalism at finite temperature. Note, that without an external magnetic field the average magnetization is zero, $\langle M \rangle = 0$. We calculate the magnetic susceptibility $\chi_{ij}(\omega, k)$, as a function of (real) frequency $\omega$ and a wave vector $k$ as given by the Kubo formula

$$\chi_{ij}(\omega, k) = \frac{1}{\pi} \left[ \int_0^\infty d\tau e^{i\omega \tau} \langle [M_i(r,t), M_j(0)] \rangle \right].$$

(5)

Here $\omega_\omega = \omega + i\delta$, $[,]$ is a commutator and $\langle \cdot \cdot \cdot \rangle$ is the thermal average, with the temperature in terms of the electric polarization as given by equation (1). Furthermore, the polarization created by the long wave optical phonons reads as [25]

$$P_i = \frac{1}{\sqrt{V}} \sum_{q\xi} A_q \gamma_{ij \xi} [\bar{b}_{\xi q} e^{i q \cdot r} + b_{\xi q} e^{-i q \cdot r}],$$

(6)

where $\gamma_{ij}$ is a piezoelectric tensor, $h_{\xi q}$ is a unit vector of a phonon polarization, index $\xi$ labels different phonon polarizations, $A_q = \sqrt{\hbar c_0^2 / 2M_\omega_\omega(q)}$, $\omega_\omega(q)$ is the phonon frequency, $c_0$ is the lattice spacing, $M_0$ is the reduced mass of the two atoms in the unit cell, and $b_{\xi q}$ ($\bar{b}_{\xi q}$) are annihilation (creation) phonon operators. For simplicity, we consider a case when the tensor $\gamma_{ij} = \gamma \delta_{ij}$ is diagonal which corresponds to a cubic crystal system. Using equation (5) we then find

$$\chi_{ij}(\omega, k) = -\delta_{ij} \sum_{q,\xi} \int \frac{d\omega_+ + \zeta N(\omega_\omega | q - k)}{s_q} \int \frac{d\omega_- + \zeta N(\omega_\omega | q + k)}{s_q},$$

(7)

where $s_q \equiv \int d^3q / (2\pi)^3$, $\omega_\pm = \omega + i\delta$, and $\Lambda = (16/9)A_0^2 h (\hbar c_0^2 / M_0)^2$. The details of the calculations are presented in the supplemental material (SM (https://stacks.iop.org/JPCM/33/04LT01/mmedia)) [26]. Note that the result is proportional to the Bose distribution function $N(\omega_\omega)$. The zero temperature contribution is discussed in the footnote [27]. By using expression for $\lambda$ from equation (1) and the estimate $\gamma \approx c_+ / a_0^2$ [25], the quantity $\Lambda$ can be expressed as $\Lambda \approx (e_+ / M_0) c_+^2 / \hbar \approx \mu_0 / \hbar$, where we have assumed that $(m_+ - m_-) / (m_+ + m_-) \approx 1$. Therefore, the magnetic susceptibility in equation (7) scales with the nuclear magneton.

To illustrate the result in equation (7), we first consider the case when the system is far from the QCP deep into the paraelectric phase, and the dispersion of the transverse optical phonons is given by equation (2) with a fixed gap $\omega_0$ and the transverse sound velocity $s_0$. Moreover, we will assume that the temperature is low enough, $T \ll \hbar \omega_0$, implying that the corresponding thermal momentum $q_T \ll \omega_0 / s_0$, with $q_T \approx \sqrt{T c_0^2 / \hbar}$ (12/3). Expanding at small momenta $k \ll q_T$, after performing the angular integration, we obtain [26]

$$\chi(\omega, k) \approx \frac{\hbar^2}{a_0^2} \int_0^{\infty} \frac{dq}{2\pi^2} \frac{q^2 N(\omega_\omega(q))}{\omega_\omega(q)^2 - (\omega + i\delta)^2/k^2}. $$

(8)

The denominator of the function in equation (8) is the difference between a square of a phase velocity of the external probe, $\omega / k$, and a square of a group velocity of a phonon at a given momentum $q$, $v_g(q) = s_0^2 q / \omega_0$. The characteristic group velocity of a phonon is $v_g(T) \approx s_0 \sqrt{T / \hbar \omega_0}$, obtained at $q = q_T$. Therefore, considering the case $k \ll q_T$, $T \ll \hbar \omega_0$, we find from equation (8) the imaginary part of the susceptibility in the form

$$\Im(\chi)(\omega, k) \approx \frac{\hbar^2}{a_0^2} \int_0^{\infty} \frac{dq}{2\pi^2} \frac{q^2 N(\omega_\omega(q))}{\omega_\omega(q)^2 - (\omega + i\delta)^2/k^2},$$

(9)

while for the real part, up to corresponding higher order corrections, we obtain,

$$\Re(\chi)(\omega, k) \approx \frac{\hbar^2}{a_0^2} \int_0^{\infty} \frac{dq}{2\pi^2} \frac{q^2 N(\omega_\omega(q))}{\omega_\omega(q)^2 - (\omega + i\delta)^2/k^2},$$

(10)

Note that $\Re(\chi)(0, k)$ coincides with the dc result of Dzyaloshinskii and Mills, see equation (12c) in reference [3].

Vicinity of the QCP. We now consider the magnetic susceptibility near the FE QCP where the phonon spectrum assumes the form as in equation (2). Furthermore, in the close proximity of the QCP, $|1 - \delta| = |1 - \nu| = \approx 1$, and $\delta$ is small compared to the scale set by temperature, $\omega_\omega(q_T)(1 - \delta)^2 \ll T$. The main contribution to the integral in equation (7) then arises from the energies $\approx T$, when the spectrum $\omega_\omega(q) \approx s_0 (q) / \hbar$ (we here neglect anomalous dimension of ferroelectric fluctuations, i.e. $\eta = 0$). At small momenta $k \ll q_T = T / \hbar s_0$, using equation (7), we then obtain

$$\Im(\chi)(\omega, k) \approx \frac{\hbar^2}{a_0^2} \int_0^{\infty} \frac{dq}{2\pi^2} \frac{q^2 N(\omega_\omega(q))}{\omega_\omega(q)^2 - (\omega + i\delta)^2/k^2}, $$

(12)

where $\theta(x)$ is the step function. This result, together with the Kramers–Kronig relations, yields the following form of the real part of the susceptibility

$$\Re(\chi)(\omega, k) \approx \frac{\hbar^2}{a_0^2} \int_0^{\infty} \frac{dq}{2\pi^2} \frac{q^2 N(\omega_\omega(q))}{\omega_\omega(q)^2 - (\omega + i\delta)^2/k^2}. $$

(13)

Importantly, in the limit of the zero frequency, we then obtain

$$\Re(\chi)(0, k \rightarrow 0) \approx \frac{\hbar^2}{a_0^2} \int_0^{\infty} \frac{dq}{2\pi^2} \frac{q^2 N(\omega_\omega(q))}{\omega_\omega(q)^2 - (\omega + i\delta)^2/k^2}. $$

(14)
with $\Lambda \simeq \mu_N^2 / h$, see equation (7). We therefore find a strong increase of the susceptibility in the close proximity of the FE QCP due to the vanishing phonon velocity, $z > 1$.

Estimates and experimental proposal. Let us estimate the magnitude of the magnetic susceptibility, equation (14), in the case of bulk SrTiO$_3$. We consider first the case when the system is far from the QCP, taking $s_0 = s_0$. From the experimental data of reference [16] one can estimate $s_0 \approx 3 \times 10^5$ cm$^{-1}$. Then taking $M_0 \approx 12m_p$, $e_+ = 4|e|$, and $T = 50$ K we obtain $\chi(\omega = 0) \simeq 10^{-11}$. If one takes $1 - \delta \simeq 0.1$, we obtain for the susceptibility near the QCP the value $\chi(\omega = 0) \simeq 10^{-9}$. Both values are experimentally measurable.

STO may be a suitable candidate material for the observation of magnetic signatures on tuning towards the FE QCP because of its incipient ferroelectric nature [28]. Similarly, KTaO$_3$, due to its incipient ferroelectric features [29], is also expected to exhibit this phenomenon. Several methods are used for tuning STO towards the FE QCP, such as strain, applied pressure [17, 18] or $^{18}$O substitution [19–22]. Biaxial strain in STO thin films, for example, can confine polarization to the plane perpendicular to the tetragonal $c$ axis but leaves undetermined the polarization direction. This creates a favorable condition for the observation of the magnetic signatures proposed here since it allows strong fluctuations between different in-plane directions of the polarization.

As for the method of tuning STO towards the FE QCP with the use of the oxygen isotope-exchange samples, we should mention here two beautiful experiments [21, 22], where the authors demonstrated the ideal softening of the ferroelectric modes at finite temperature $T_c$. To observe the effect proposed in this work, the magnetic susceptibility should be measured as a function of temperature in the close proximity of the phase transition point. A simple experimental setup consists of an SQUID placed above an STO sample.

Conclusions—Multiferroicity as a static phenomenon is well established. On the other hand, the dynamically induced multiferroic phenomena are new and there has been no experiments that explicitly prove it. In this paper, we provide the theoretical estimates and rigorous bounds on the strength of the effect. Furthermore, we have expanded the framework of dynamic multiferroicity and predict strongly enhanced magnetic susceptibility in a paraelectric material near its FE QCP due to thermal fluctuations of the electric dipoles associated with a soft optical mode driving the transition. The predicted effect indicates an alternative way for entangled quantum orders to be induced at finite temperature. We thus further support the concept, proposed in reference [4], that any FE QCP is an inherent multiferroic QCP with entangled ferroelectric and ferromagnetic fluctuations. Finally, we have considered STO as a system that can be tuned towards its FE QCP, and provided an estimate of a magnetic susceptibility for this material. The predicted value could be experimentally accessible. One of the possibilities to observe magnetic signatures of fluctuating dipoles is to make SQUID measurements.

Acknowledgments

We are grateful to K Dunnett, N Spaldin, I Sochnikov, B Spivak, J-X Zhu, C P Opeil and A Polkovnikov for useful discussions. The work was supported by VILLUM FONDEN via the Centre of Excellence for Dirac Materials (Grant No. 11744), Knut and Alice Wallenberg Foundation and the European Research Council ERC-2018-SyG HERO. VJ acknowledges the support of the Swedish Research Council (VR 2019-04735).

ORCID iDs

Alexander Khaetskii https://orcid.org/0000-0003-4017-5780

References

[1] Juraschek D M, Fechner M, Balatsky A V and Spaldin N A 2017 Dynamical multiferroicity Phys. Rev. Mater. 1 014401
[2] Rebane Y T 1983 Faraday effect produced in the residual-ray region by the magnetic moment of an optical phonon in an ionic crystal Sov. Phys. JETP 57 1356
[3] Dzyaloshinskii I E and Mills D L 2009 Intrinsic paramagnetism of ferroelectrics Phil. Mag. 89 2079
[4] Dunnett K, Zhu J-X, Spaldin N A and Juričić V and Balatsky A V 2019 Dynamic multiferroicity of a ferroelectric quantum critical point Phys. Rev. Lett. 122 057208
[5] Khmel’nik G E and Shneerson V L 1973 Phase transitions of the displacement type in crystals at very low temperatures Sov. Phys. JETP 37 164
[6] Rowley S E, Spalek I, J, Smith R P, Dean M P M, Ioth M, Scott J F, Lonzarich G G and Saxena S S 2014 Ferroelectric quantum criticality Nat. Phys. 10 367
[7] Chandra P, Lonzarich G G, Rowley S E and Scott J F 2017 Prospects and applications near ferroelectric quantum phase transitions: a key issues review Rep. Prog. Phys. 80 112502
[8] Rechester A B 1971 Contribution to the theory of second-order phase transitions at low temperatures Sov. Phys. JETP 33 423
[9] Khmel’nik G E and Shneerson V L 1973 Zh. Eksp. Teor. Fiz. 64 316
[10] Rowley S E, Spalek I, J, Smith R P, Dean M P M, Ioth M, Scott J F, Lonzarich G G and Saxena S S 2014 Ferroelectric quantum criticality Nat. Phys. 10 367
[11] Rechester A B 1971 Zh. Eksp. Teor. Fiz. 60 782
[12] Rouasse R and Millis A J 2003 Theory of the quantum paraelectric-ferroelectric transition Phys. Rev. B 67 014105
[13] Sondhi S L, Girvin S M, Carini J P and Shahar D 1997 Continuous quantum phase transitions Rev. Mod. Phys. 69 315
[14] Sachdev S 2011 Quantum Phase Transitions 2nd edn (Cambridge: Cambridge University Press)
[15] Edge J M, Kedem Y, Aschauer U, Spaldin N A and Balatsky A V 2015 Quantum critical origin of the superconducting dome in SrTiO$_3$ Phys. Rev. Lett. 115 247002
[16] Rischa C W et al 2017 A ferroelectric quantum phase transition inside the superconducting dome of Sr$_{1-x}$Ca$_x$TiO$_3$−δ Nat. Phys. 13 643
[17] Narayan A, Cauza A, Balatsky A V and Spaldin N A 2018 Multiferroic quantum criticality Nat. Mater. 18 223–8
[18] Arce-Gamboa J and Gutzmín-Verrini G 2018 Quantum ferroelectric instabilities in superconducting SrTiO$_3$ Phys. Rev. Mater. 2 104804
[19] Yamada Y and Shirane G 1969 Neutron scattering and nature of the soft optical phonon in SrTiO$_3$ J. Phys. Soc. Japan 26 396
[20] Burke W J and Pressley R J 1971 Stress induced ferroelectricity in SrTiO$_3$ Solid State Commun. 9 191
[18] Uwe H and Sakudo T 1976 Stress-induced ferroelectricity and soft phonon modes in SrTiO₃ Phys. Rev. B 13 271

[19] Itoh M, Wang R, Inaguma Y, Yamaguchi T, Shan Y-J and Nakamura T 1999 Ferroelectricity induced by oxygen isotope exchange in strontium titanate perovskite Phys. Rev. Lett. 82 3540

[20] Wang R and Itoh M 2001 Suppression of the quantum fluctuation in 18O-enriched strontium titanate Phys. Rev. B 64 174104

[21] Takesada M, Itoh M and Yagi T 2006 Perfect softening of the ferroelectric mode in the isotope-exchanged strontium titanate of SrTi18O3 studied by light scattering Phys. Rev. Lett. 96 227602

[22] Taniguchi H, Itoh M and Yagi T 2007 Ideal soft mode-type quantum phase transition and phase coexistence at quantum critical point in 18O-exchanged SrTiO3 Phys. Rev. Lett. 99 017602

[23] Ghosez P, Cockayne E, Waghmare U V and Rabe K M 1999 Lattice dynamics of BaTiO3, PbTiO3, and PbZrO3: a comparative first-principles study Phys. Rev. B 60 836 Notice that the velocities near the zone center of the (unstable) soft phonon modes obtained by first-principle calculations are anomalously small

[24] In the case $T \ll \hbar \omega_0$ we should additionally take into account the exponentially small number of the excited phonons, $N \propto \exp(-\hbar \omega_0/T)$. In this case the density of states is $\rho(T) \approx q^3/T \approx T^{1/2} \omega_0^2 (\sqrt{(\hbar s_\perp)})^3$, where we use that $\omega_\perp(q_T) \approx \omega_0 \approx (s_\perp q^2 2 \omega_0) \approx T/\hbar$. Then the product of three terms, $\mu \omega_0 \exp(-\hbar \omega_0/T)$, and $\rho(T)$, gives the result in agreement with the one obtained more formally, which is displayed in equation (10)

[25] Gantmakher V F and Levinson Y B 1987 Carrier Scattering in Metals and Semiconductors (Amsterdam: North-Holland)

[26] See supplemental material for the technical details of the derivation of the form of the susceptibility in equation (8)

[27] The zero temperature contribution can be estimated as $\Re \chi(0, k \to 0) \approx \Lambda(k^2/s_\perp) \ln(1/q^* a_0)$. $q^* a_0 \ll 1$. The characteristic phonon wave vector $q^* \approx \omega_0(\delta)/s_\perp(\delta)$ is determined by the gap and the transverse sound velocity at a given distance from the QCP, given by the tuning parameter $\delta$. Since we consider the limit $k \to 0$, we neglect this contribution. Notice that this zero temperature estimate is obtained with the use of the bare Greens’ function for the soft phonons. In the quantum critical region the problem should be solved by accounting for the proper self-energy corrections to the phonon propagator and is the subject of the future investigation

[28] Müller K A and Burkard H 1979 SrTiO3: an intrinsic quantum paraelectric below 4 K Phys. Rev. B 19 3593

[29] Perry C H and McNelly T F 1967 Ferroelectric ‘soft’ mode in KTaO3 Phys. Rev. 154 456