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Critical behavior of the order parameter at antiferrodistortive transitions with cubic fluctuations

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The temperature dependence of the generalized order parameter, namely the rotation angle of the NbO_6 octahedron, at the antiferrodistortive transition in the perovskite crystal $NaNbO_3$, is derived through the high-resolution analysis of the second-order quadrupole shift of ^{23}Na NMR spectra. The second-order character of the transition and the small value of the apparent critical exponent for the order parameter are critically discussed in the framework of a renormalization-group approach for a system with an effective Hamiltonian of cubic symmetry and an anisotropic dispersion in the static structure factor.

I. INTRODUCTION

Certain antiferrodistortive phase transitions in perovskite crystals in the presence of sufficiently strong cubic anisotropy, which are predicted second order within the mean-field approximation, are expected to be first order in the framework of theoretical descriptions based on the renormalization-group approach.[1] In fact a cubic- or lower-symmetry perturbation drives the renormalized Hamiltonian out of the range of thermodynamic stability, destroying the continuous character of the transition. In certain cases a suitable symmetry-breaking field, as an appropriate anisotropic stress, restores the continuity and a tricritical point is exhibited. Moreover, a complete flatness of the soft mode between the R and M points of the Brillouin zone, namely two-dimensionally correlated fluctuations, can possibly lead to the Lifshitz behavior.[2] More recently, also the possibility that fluctuations turn first-order transitions into second order has been considered.[3] In the light of the above-mentioned problematics some experimental and theoretical attention has recently been devoted to the cubic-to-tetragonal structural transition occurring in perovskite crystals ABO_3 and involving rotational antiferrodistortive tilts of the BO_6 octahedra around the principal cubic axes. In $NaNbO_3$, in particular, x-ray diffraction,[4] neutron scattering[5] and NMR studies[6] indicate that for $T \gtrsim T_c + 10$ K the transition is driven by the softening of a large part of the branch from the R point to M point, corresponding to rotational fluctuations only two dimensionally (2D) correlated within parallel planes. For temperature closer to $T_c \simeq 910$ K a crossover between 2D and 3D behavior of the fluctuations occurs,[5] with the onset of a ferrodistortive ordering among adjacent planes, namely freezing-in of a pure M_3 mode.

NMR quadrupole perturbed spectra are often ideal tools to investigate the temperature behavior of the local order parameter, i.e., the angle of rotation ϕ of the octahedral units.[7] In particular, the second-order shift of the central NMR line due to the static electric field gradient (EFG) at the resonant nucleus below T_c has been used in some cases.[6,8,9]

In $NaNbO_3$, some insights could be achieved[6] through the behavior of the free-induction decay due to the second-order quadrupole broadening of the central line ($+\frac{1}{2} \leftrightarrow -\frac{1}{2}$ transition) in a powdered sample. However, the lack of frequency resolution made it difficult to carry out a detailed analysis of the critical region through the data of that early investigation.[6]

The subsequent theroetical developments,[1,3] the availability of a large single crystal of $NaNbO_3$ (kindly provided by F. Denoyer and R. Comes, Orsay), and finally significant improvement in the Fourier-transform (FT) pulse NMR techniques and related data processing recommended a further study of the critical behavior of $\phi(T)$ in $NaNbO_3$. The opportunity for such a study is also corroborated by the fact that the critical analysis of the theoretical predictions,[1,3] until now, has been performed essentially only through EPR measurements in $RbCaF_3$ doped with Gd^{3+}.[10] On the other hand, it can be suspected that doping conveys information of partially extrinsic character (local strains and/or impurity centers).

This Brief Report deals with the results of a careful experimental investigation of the temperature behavior of the order parameter ϕ in the critical region in $NaNbO_3$. This behavior is discussed in the light of the renormalization-group predictions for a system with an effective Hamiltonian containing a perturbation of cubic symmetry and for an anisotropic static structure factor.

II. EXPERIMENTAL RESULTS

The NMR measurements have been performed at about 22 MHz by means of a SPX Bruker coherent

pulse spectrometer. The rf amplitude was about 80 G. The transient free-induction decays were averaged over 10^3 accumulations and then Fourier transformed by a Nicolet B-NC 12 data processor system. A feedback-controlled furnace properly designed could maintain a temperature stability better than 0.1 K (10^{-5} in reduced temperature) for the time of a complete series of collections. The temperature gradients at the sample were less than 0.1 K along the larger dimension of the crystal (approximately 1 cm). The single crystal of $NaNbO_3$ was oriented with a cubic axis parallel to the rf field and then rotated around this axis so that the maximum separation between the resonance lines was detected. This allows one to achieve the best frequency resolution (see below). In the tetragonal phase a nonzero EFG arises at the Na site due to the rotations of the NbO_6 octahedra and the slight tetragonal distortion of the cell. In a point-charge model, taking into account only the displacements of the nearest-neighbor oxygen, sodium, and niobium atoms, one finds for the EFG

$$V_{zz}=[2e(1-\gamma_\infty)/a^3](6\sqrt{2}\phi+6.6\phi^2) \ , \qquad (1)$$

with an asymmetry parameter $\eta=1-1.6\phi$ (rotation angle ϕ in rad). In Eq. (1), $a=3.94$ Å is the lattice parameter of the pseudocubic cell, $\gamma_\infty=-4.8$ the Sternheimer antishielding factor.

The nonzero EFG perturbs the Zeeman levels and the satellite lines ($\pm\frac{3}{2}\leftrightarrow\pm\frac{1}{2}$ transitions) cannot be detected because their first-order smearing in a large frequency range, possibly as a result of strains. The central line ($+\frac{1}{2}\leftrightarrow-\frac{1}{2}$ transition) is affected only to second order and it can be detected. The transition temperature was located from the disappearance of the contribution to the free induction decay signal from the satellite transitions. It was found $T_c=909\pm0.2$ K.

The second-order quadrupole shift of the central line results in

$$\Delta\nu_{1/2}^{(2)}=-\frac{\nu_Q^2}{2\nu_L}f_\eta(\theta,\phi) \ ,$$

where $\nu_Q=eQV_{zz}/2h$ is the quadrupole coupling constant and $f_\eta(\theta,\phi)$ is an angular function whose expression will not be given here. Because of the three possible domains with perpendicular orientations of the tetragonal c axis, there central lines are observable, in general. For a crystal with a pseudocubic axis perpendicular to $\vec{H}_0$ and $\eta\simeq1$, two lines are pratically superimposed. Only two lines are then observed, the frequency separation being

$$\Delta\nu=\frac{\nu_Q^2}{16\nu_L}|2-\cos2\delta+9\sin^2 2\delta| \ ,$$

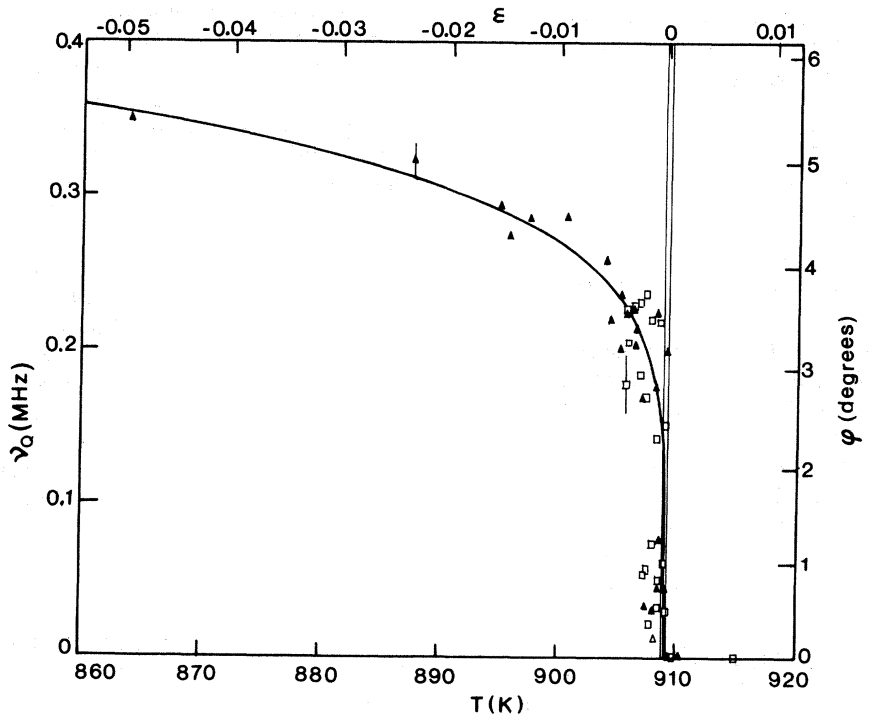

FIG. 1. ^{23}Na quadrupole coupling constant ν_Q and the corresponding angle of rotation of the oxygen octahedra [derived according to Eqs. (1) and (2) and in the text] as a function of temperature. (□ for decreasing temperature, ▲ for increasing temperature). The vertical lines indicate the transition temperature $T_c=909\pm0.2$ K, with the experimental uncertainty. The solid line is the best fit of the data according to a power law of the form $\phi(T)\propto\epsilon^\beta$, with $\beta=0.17\pm0.02$. (See text.)

where δ is the angle between $\vec{H}_0$ and a pseudocubic axis. The highest resolution attainable is

$$\Delta\nu = \frac{10.77}{16}\frac{\nu_Q^2}{\nu_L} \tag{2}$$

for $\delta \simeq 0.73$ rad. In the presence of broadening of the lines due to dipolar interactions and field inhomogeneity, the spectrum appears as the surposition of two Gaussians of equal width. The modulus of the FT, instead of the real part, was generally recorded in order to overcome the problems related to the phase correction. Near the critical temperature, where the separation lines are not well resolved, a careful computer analysis of spectra was necessary. The frequency separation of the lines was obtained by means of a nonlinear six-parameters least-squares fit for the modulus of the FT of a sum of two Gaussians. The best fit was performed by parabolic extrapolation of χ^2 and generally it appears rather good. From Eq. (2) ν_Q was derived as a function of temperature (see Fig. 1). No sizeable difference appeared between the data obtained on heating and those on cooling, thus indicating the lack of sizeable hysteresis effects.

III. ANALYSIS OF THE DATA AND DISCUSSION

To describe the cubic to tetragonal transition in $NaNbO_3$ one can refer to the Hamiltonian $\mathcal{H} = \int d^dx\, \mathcal{H}$, $\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_c$, where

$$\mathcal{H}_0 = \tfrac{1}{2}|\nabla\vec{\varphi}|^2 + \tfrac{1}{2}r|\vec{\varphi}|^2 + u_4|\vec{\varphi}|^4 \ , \tag{3}$$

with $u_4 > 0$ and $r \propto (T - T_0)$ is the usual Landau-Ginzburg-Wilson (LGW) isotropic Hamiltonian, while

$$\mathcal{H}_c = \sum_\alpha [\tfrac{1}{2}f(\partial_\alpha\varphi^\alpha)^2 + g(\partial_\alpha^2\varphi^\alpha)^2 + v(\varphi^\alpha)^4] \tag{4}$$

with $v < 0$, accounts for the cubic symmetry. $\varphi^\alpha(\vec{x})$ denotes the rotational angle around the n crystalline cubic axis and $n = d = 3$: for instability at the R point φ^α are staggered rotational angles; in the case of a M-point instability φ^α are staggered only in the plane perpendicular to the α axis. In Eq. (4) the last term yields the tetragonal symmetry, while the first two correspond to the anisotropic dispersion Δ_α of the soft branch, which for $f = 1$ describes a Lifshitz point:

$$\Delta_\alpha = r + q_{\perp\alpha}^2 + gq_\alpha^4 \quad (q_{\perp\alpha}^2 = q^2 - q_\alpha^2) \ .$$

When a stable fixed point is accessible by the LGW Hamiltonian the phase transition is expected to be second order. When under renormalization-group transformation this Hamiltonian flows to a region in its parameter space where it becomes thermodynamically unstable, a first-order transition should occur, which is said[1] to be driven first order by the critical fluctuations. This could be expected to be the case in $NaNbO_3$, primarily in view of the similarity with $RbCaF_3$.[1,10]

The data reported in Fig. 1 indicate that the temperature dependence of φ is pratically continuous. Attempts to fit the data by imposing a limiting temperature T_0 slightly different from T_c give poor fits. it is worthwhile to stress that the second-order character of the transition is strongly corroborated by the *gradual* disappearing of the contribution from the satellite lines ($\pm\frac{1}{2} \leftrightarrow \pm\frac{3}{2}$ transition) to the signal below the transition. A power law of the form $\varphi \propto \epsilon^\beta$ appears to fit the data properly and yields an apparent critical exponent $\beta = 0.17 \pm 0.02$, in the whole range of reduced temperature $0 \lesssim \epsilon \lesssim 0.05$.

The continuous character of the transition and the small value of β could be attributed, in principle, to the occurrence of internal anisotropic stress. Stresses act like a symmetry-breaking field and can be described by a Hamiltonian of the form

$$\mathcal{H}_g = \frac{1}{2}\frac{w}{n}\left[(n-m)\sum_{\alpha=1}^{m}\varphi_\alpha^2 - m\sum_{\alpha=m+1}^{n}\varphi_\alpha^2\right] \ , \tag{5}$$

which reduces the effective number of components of $\vec{\varphi}$ from n to m (or $n - m$ depending on the sign of w). This crossover of dimensionality of the order parameter brings the Hamiltonian into the domain of a new stable fixed point, yielding a second-order transition. However, the occurrence of sizable stress *above* T_c can be ruled out. In fact, as already mentioned, in the high-temperature region the satellite lines, which are sensitive at the first order, through the electric field gradients, to the stress, still contribute to the ^{23}Na NMR signal.

A possibility to take into consideration is the case of vanishing small w in Eq. (5) with the addition in the isotropic Hamiltonian [Eq. (3)] of higher-order terms of the form $\mathcal{H}' = u_6|\vec{\varphi}|^6$, with u_4 and u_6 positive and sufficiently large. This is one of the situations recently considered by Blankschtein and Aharony[3] and for which second-order phase transitions occur. In this case $NaNbO_3$ would represent the first experimental indication, in the authors' knowledge, of a zero-stress bicritical behavior in the presence of anisotropic cubic fluctuations.

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[1]A. Aharony and A. D. Bruce, Phys. Rev. Lett. 42, 426 (1979); A. Aharony, in *Proceedings of the Thirteenth International Union of Pure and Applied Physics Conference on Statistical Physics, Haifa, Israel, 1977,* edited by D. Cabib, C. G. Kujer, and I. Riess (Annals of the Israel Physical Society, Haifa, Israel, 1978), Vol. 1, p. 13.

[2]R. M. Hornreich, M. Luban, and S. Shtrikman, Phys. Rev. Lett. 35, 1678 (1975).

[3]D. Blankschtein and A. Aharony, Phys. Rev. Lett. 47, 439 (1981).

[4]R. Comes, R. Currat, F. Denoyer, M. Lambert, and A. M. Quittet, Ferroelectrics 12, 3 (1976).

[5]F. Denoyer, M. Lambert, R. Comes, and R. Currat, Solid State Commun. 18, 441 (1976).

[6]A. Avogadro, G. Bonera, F. Borsa, and A. Rigamonti, Phys. Rev. B 9, 3905 (1974).

[7]For a review see, F. Borsa and A. Rigamonti, in *Magnetic Resonance of Phase Transitions,* edited by F. J. Owens, C. P. Poole, and H. A. Farach (Academic, New York, 1979); A. Rigamonti, in *Structural Phase Transition,* edited by H. Thomas and K. A. Müller (Springer-Verlag, Berlin, 1982).

[8]S. V. Bhat, P. P. Mahendroo, and A. Rigamonti, Phys. Rev. B 20, 1812 (1979).

[9]F. Borsa, Phys. Rev. B 7, 913 (1973).

[10]J. Y. Buzaré, J. C. Fayet, W. Berlinger, and K. A. Müller, Phys. Rev. Lett. 42, 465 (1979); J. Y. Buzaré, M. Fayet-Bonnel, and J. C. Fayet, J. Phys. C 13, 857 (1980); see also, K. A. Müller, W. Berlinger; J. Y. Buzaré and J. C. Fayet, Phys. Rev. B 21, 1763 (1980).