[14]J. di Persio, J. C. Doukhan, and G. Saada, Mater. Sci. Eng. 4, 123 (1969).
[15]J. C. Doukhan and J. L. Farvacque, Phys. Status Solidi (a) 14, 623 (1972).
[16]A. M. Kosevich and L. V. Tanatarov, Fiz. Tverd. Tela 6, 3423 (1964) [Sov. Phys. Solid State 6, 2738 (1965)].
[17]E. A. Kaner and E. P. Feldmann, Zh. Eksp. Teor. Fiz. 58, 1603 (1970) [Sov. Phys. JETP 31, 966 (1970)].
[18]For a recent review see H. R. Zeller, in *Festkörperprobleme*, edited by H. J. Queisser (Pergamon, New York, 1973), Vol. XIII.
[19]Y. Alpert and C. Rigaux, Solid State Commun. 5, 391 (1967).

Critical Dynamics in $SrTiO_3$ from Paramagnetic Resonance

K. A. Müller, W. Berlinger, C. H. West, and P. Heller*
IBM Research Laboratory, CH-8803 Rüschlikon, Switzerland
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Paramagnetic resonance line shapes and linewidths of the Fe^{3+}-V_0 center in $SrTiO_3$ above T_c permit the determination of an effective relaxation rate $\Delta\omega_l(T)$ for the local rotations of the oxygen octahedra by observation of the crossover from Lorentzian to Gaussian line shapes with different settings of the applied field. We find that $\Delta\omega_l$ decreases as $T \to T_c^+$, clearly indicating critical slowing down. In addition, the relaxation rate Γ_c for the R-point (order-parameter) collective mode is estimated from the linewidths in the region of Lorentzian shapes, indicating a "central peak" of width $\Gamma_c \approx 0.6 \times 10^8$ sec$^{-1} \approx 0.1\Delta\omega_l$ at $T = T_c + 2$ K.

The dynamic behavior near a structural phase transition is of considerable current interest.[1-3] In this Letter we investigate by EPR techniques the critical slowing down of rotational fluctuations of oxygen octahedra in $SrTiO_3$ above its antiferrodistortive phase transition. Our results provide quantitative information on how the *local* relaxation rate $\Delta\omega_l$ changes with temperature. Furthermore, we estimate the width of the "central peak" $\Gamma_c(T)$ dominating the *collective* scattering function $S(q, \omega)$ near T_c at the wave vector $q_R = \pi/a(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ of the condensing soft mode. This has been observed with inelastic neutron scattering near antiferrodistortive phase transitions but its frequency width could not be resolved.[4-6] This observation has been the subject of numerous theoretical treatments[7,8] including a computer "experiment."[9]

In $SrTiO_3$ the EPR of the Fe^{3+}-V_0 center can be used as a sensitive probe to investigate the local rotation angles φ_l^α about a given axis $\alpha = \langle 001\rangle$ when the applied field $\vec{H}$ and the center axis are in a (001) plane.[10] There the resonance magnetic field is given by $H_r = H_0 + A\varphi_l^\alpha$, where $H_0 = \hbar\omega/g_{\text{eff}}\beta$. The dependence of g_{eff} and $A = \partial H_r/\partial\varphi_l^\alpha$ on angle θ between $\vec{H}$ and the center axis has been determined.[10]

As $T \to T_c$, the φ_l^α fluctuations result in a pronounced broadening of the linewidth ΔH.[11] This provides information on the local autocorrelation function $G^{\alpha\alpha}(t) = \langle \delta\varphi_l^\alpha(t)\,\delta\varphi_l^\alpha(0)\rangle$ or, equivalently, the local rotation spectral density

$$J_l(\omega) = (2\pi)^{-1}\int_{-\infty}^{+\infty} G^{\alpha\alpha}(t)e^{i\omega t}\,dt = N^{-1}\textstyle\sum_q S(q, \omega). \tag{1}$$

Two limiting regimes of behavior are expected depending on whether the φ_l fluctuations are slow or fast in comparison with the magnetic relaxation $\Delta\omega$ they produce.[11,12] For very slow fluctuations the line shape is proportional to the probability $P(\varphi_l)$ to observe φ_l,[13] which may be a Gaussian distribution, giving a linewidth

$$\Delta H \simeq 2A\langle\delta\varphi_l^2\rangle^{1/2} = 2A\left[\int_{-\infty}^{+\infty} J_l(\omega)\,d\omega\right]^{1/2}. \tag{2}$$

In this regime most of the area under $J_l(\omega)$ is concentrated at frequencies small compared with the resulting EPR linewidth $\Delta\omega = \Delta H g_{\text{eff}}\beta/\hbar$. In the fast-motion limit, where $J_l(\omega)$ is spread out over a range wide compared to $\Delta\omega$, the observed lines should be Lorentzian in shape, and of width ΔH proportional to $J_l(0)$. More particularly, the angular frequency width between derivative extrema should then be

$$\Delta\omega = (2\pi/\sqrt{3})B^2 J_l(0). \tag{3}$$

Here $B = g_{\text{eff}}\beta A/\hbar$ is the parameter which measures the coupling of the instantaneous local EPR frequency to the corresponding rotation angle.

Now $J_l(0)$ should diverge as $\Delta T = T - T_c$ approaches zero, while $\langle \delta\varphi_l^2\rangle^{1/2}$ remains finite. Hence as $\Delta T \to 0$, a "crossover" manifests itself in two ways: (a) The temperature dependence of $\Delta\omega$ should change from a relatively steep behavior at large ΔT, to a relatively flat behavior at small ΔT. Concurrently, (b) the line shapes, Lorentzian at large ΔT, should become more Gaussian for small ΔT.

Experimentally, a temperature-dependence crossover as predicted in (a) was indeed seen in $SrTiO_3$ with EPR[11] and more recently in $NaNbO_3$ with NMR.[14] A preliminary observation of line-shape crossover (b) was also reported.[13,15] The present experiments, undertaken in an effort to study these critical dynamics more quantitatively, are based on the following idea: Suppose we were to increase the value of the coupling parameter $B(\theta)$; then the EPR would broaden sooner as $T \to T_c^+$, with line-shape crossover also taking place at a higher temperature. We sought to determine whether this crossover took place at a larger value of the *linewidth*. This must be the case if the local fluctuations slow down for decreasing ΔT.

In practice, the coupling parameter was varied by changing the angle θ between $\vec{H}_0$ and [100] in the (001) plane. For θ near 15°, B has a maximum value of 9.7×10^{10} sec^{-1}/rad, and decreases by a factor of $\simeq 1.6$ at $\theta = 45°$. Experimentally, the linewidth $\Delta H(T)$ was determined at 0.25- to 1-K intervals for $\theta = 32°$, 25°, and 15°, and we used the data for $\theta = 45°$, i.e., the [110] direction, from Ref. 12. The background width was subtracted off as indicated there. For $\theta = 15°$ and 45° the field-derivative line profile $f'(H)$ was sampled at a series of temperatures. The data were least-squares fitted by a sum of normalized Lorentzian and Gaussian shapes. The percentage p or $100 - p$, respectively, could be determined to within 5%.

In Fig. 1 we plot the values of $\Delta\omega(T)$ computed from the measured linewidth $\Delta H(T)$ versus ΔT for each θ value. The gradual line-shape change along each curve is shown by the points in percentages of Lorentzian contribution p. The oblique dashed lines form the loci of similar line shapes. These lines have positive slope. This indicates that a given degree of crossover, when attained at a higher temperature, is attained at a larger linewidth. Thus the *whole figure* proves *the existence of dynamic slowing down of local fluctuations.*[16]

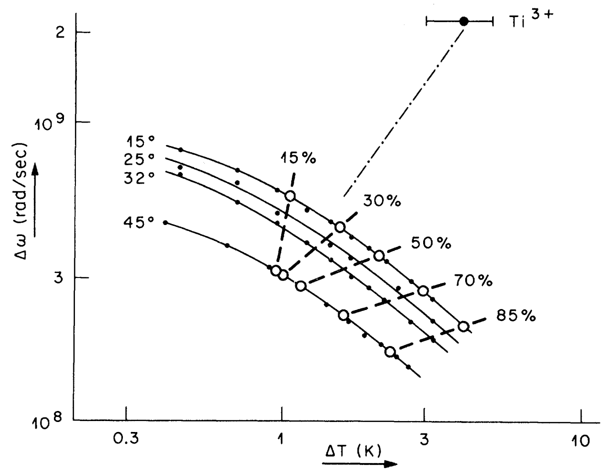

FIG. 1. Temperature dependence of the angular frequency linewidth $\Delta\omega$ for four different values of B. The percentages attached to the loci of similar line shapes (dashed lines) correspond to the Lorentzian component in the fit. The single point at the top is the $\Delta\omega_l$ estimate of Ref. 18.

One expects crossover to occur when $\Delta\omega$ is comparable to the local fluctuation rate $\Delta\omega_l$. Because the shape of $J_l(\omega)$ is unknown, no specific value for p at crossover can be given. However, from an inspection of Fig. 1, $s = d(\Delta\omega_l)/dT$ must be larger than the slope of the 50% curve s_{50}. The latter is nearly parallel to s_{85} which is situated in the fast-motion regime. From the figure the slope $s_{30} = (3.2 \pm 1.6)\times 10^8$ rad sec^{-1} K^{-1} appears to be a reasonable empirical choice for the changeover. In addition, s_{30} is close to the points on $\Delta\omega_l$ for the values of θ as they are obtained independently[17] by fitting the measured linewidth $\Delta H(T)$ by Schwabl's theory.[7] Furthermore, an estimated s_{25} extrapolates to the point resulting from an investigation of the Ti^{3+} center.[18] The latter ion is situated at an Sr^{2+} place and couples to the fluctuations. If these are slower than an experimentally given frequency $\Delta\nu = 3.5\times 10^8$ Hz an orthorhombic spectrum is seen, otherwise an axial one. The temperature dependence of the ratio of the two intensities shows a knee at $\Delta T = 4 \pm 1.0$ K, where $\Delta\omega_l(T) = 2\pi\Delta\nu$ was assumed.[18]

We now use the EPR linewidth data to estimate the rotational fluctuation rate of collective coordinate $\varphi_q(t) = (1/\sqrt{N})\sum_l \varphi_l(t)\exp[i(q_R + q)r_l]$. In terms of the structure factor $S(q,\omega)$, the local spectral density is $J_l(\omega) = V_k^{-1}\int d^3q\, S(q,\omega)$, the integral being carried out over the Brillouin zone of volume $V_k = 8\pi^3/a^3$. Then Eq. (3) becomes

$$\Delta\omega = \frac{B^2a^3}{4\pi^2\sqrt{3}} \int d^3q\, S(q,0) = \frac{B^2a^3}{4\pi^3\sqrt{3}} \int d^3q \frac{\langle \delta\varphi_q^{\,2}\rangle}{\Gamma_{\rm eff}(q)}, \qquad (4)$$

where we defined an effective relaxation rate $\Gamma_{\rm eff}(q)$ by writing $\pi\Gamma_{\rm eff}(q)S(q,0) = \int S(q,\omega)\,d\omega = \langle \delta\varphi_q^{\,2}\rangle$. We now refer to theories[5,7,8] of the damped oscillator type in which the central peak is associated with a frequency-dependent damping $\Gamma'(q,\omega) + i\Gamma''(q,\omega)$. For all modes q which contribute appreciably to the linewidth, we *assume* the following features of those theories: (i) that the T and q dependence of $\langle \delta\varphi_q^{\,2}\rangle$ is related to the renormalized phonon frequency $\omega_0(q)$ by

$$\langle \delta\varphi_q^{\,2}\rangle \propto k_B T/\omega_0^{\,2}(q) \propto k_B T[|q|^2 - (1-\Delta)q_\alpha^{\,2} + \kappa^2]^{-1};$$

(ii) that $\Gamma_{\rm eff}(q)$ approaches a finite temperature-dependent value Γ_c as $q \to 0$, and that

$$\Gamma_{\rm eff}(q)/\Gamma_c = [|q|^2 - (1-\Delta)q_\alpha^{\,2} + \kappa^2]/\kappa^2$$

[this assumption, which is really an assertion of "conventional" slowing down, is obtained in the critical region of the damped oscillator theories, where[7] $\Gamma_{\rm eff}(q) = \omega_0^{\,2}(q)/\Gamma'(q,0)$, provided that $\Gamma'(q,0)$ is assumed to depend weakly on q]; (iii) that $\omega_0^{\,2}(q) = \omega_0^{\,2}(0) + \lambda_2|q|^2 + (\lambda_1 - \lambda_2)q_\alpha^{\,2}$, where λ_1 and λ_2 are slowly varying functions of T, obtainable from neutron-scattering data.

From (i) and (iii) we have

$$\kappa^2 = \omega_0^{\,2}(0)/\lambda_2, \qquad (5a)$$

$$\Delta = \lambda_1/\lambda_2, \qquad (5b)$$

while using (i) and (ii) in Eq. (4) we find

$$\Delta\omega \simeq \frac{B^2a^3}{\pi^2\sqrt{3}} \frac{\langle \delta\varphi_{q=0}^{\,2}\rangle}{\Gamma_c} \frac{\kappa^3}{\sqrt{\Delta}} \int_0^\infty \frac{x^2\,dx}{(1+x^2)^2}. \qquad (6)$$

To obtain an expression for $\langle \delta\varphi_{q=0}^{\,2}\rangle$, consider first the situation at large ΔT where the structure factor is dominated by the phonon sidebands. There a straightforward application of the equipartition theorem shows that

$$\langle \delta\varphi_{q=0}^{\,2}\rangle = 2k_B T/M_0\omega_0^{\,2}(0)a^2, \qquad (7)$$

where M_0 is the oxygen mass and a the lattice constant. Note that in view of assumption (i), Eq. (7) should remain valid in the central peak-dominated region. Using (7) and (5a) and evaluating the integral in (6) we find

$$\frac{\Delta\omega}{B^2} = \frac{1}{2\pi\sqrt{3}} \frac{\kappa a}{\sqrt{\Delta}} \frac{k_B T}{M_0\lambda_2} \frac{1}{\Gamma_c}. \qquad (8)$$

Equation (7) is appropriate in the fast-motion (f) regime. On the log-log plot of Fig. 1 this should correspond to straight lines drawn through the $\Delta\omega$ data for large ΔT. For $\Delta T \gtrsim 2$ K, straight-line fits are possible, yielding[19]

$$(\Delta\omega/B^2)_f = [(9\pm 3)\times 10^{-14}\,\text{sec}] \times [\Delta T/(1\text{ K})]^{-0.7}. \qquad (9)$$

Closer to T_c the curves of Fig. 1 gradually bend over as they should in accordance with expectation (a). Indeed this is taking place in the region where the line shape is observed to cross over. On comparing (9) with (8), and inserting the value $\lambda_2 = 3200\ (\text{meV Å})^2 = 7.4\times 10^{11}\ \text{cm}^2/\text{sec}^2$ obtained by neutron scattering,[5] and using $k_B T \simeq 1.5 \times 10^{-14}$ erg and $M_0 = 2.66\times 10^{-23}$ g, we find

$$\Gamma_c \simeq [0.9\times 10^9\ \text{sec}^{-1}][\Delta T/(1\text{ K})]^{0.7}\kappa a/\sqrt{\Delta}. \qquad (10)$$

Although λ_2 is reasonably well determined by neutron scattering in Ref. 5 and by Stirling[20] which agree to within about 15%, Δ and especially κa are not well known. Using the data of Ref. 5 in Eq. (5a), we estimate that $\kappa a \approx 0.015$ at $T_c + 2$ K. The original data[4] gave a value higher by about a factor of 4 due to insufficient experimental resolution.[5] With regard to Δ, the neutron data of Refs. 5 and 20, respectively, yield the values 0.1 and 0.035 above T_c. Thus we can at best estimate that $\kappa a/\sqrt{\Delta}$ is of the order of 0.06 at $T_c + 2$ K. Using (10) this gives

$$\Gamma_c(T_c + 2\text{ K}) \approx 0.6\times 10^8\ \text{sec}^{-1}. \qquad (11)$$

This value is lower by a factor of 10 than the local rate $\Delta\omega_l$ at this temperature using s_{30} in the figure. This is because in the q sum that determines $J_l(\omega)$, the $q=0$ mode contributes only the slowest fluctuations. Indeed from their definitions, $\Delta\omega_l$ and Γ_c need not always be comparable and can have different temperature dependences close to T_c.

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tion under Grant No. GH 36612.

[1] *Proceedings of the NATO Advanced Study Institute on Structural Phase Transitions and Soft Modes, Geilo, Norway, April, 1971*, edited by E. J. Samuelsen, E. Anderson, and J. Feder (Universitetsforlaget, Oslo, Norway, 1972).

[2] "Proceedings of the NATO Advanced Study Institute on Anharmonic Lattices, Structural Transitions and Melting, Geilo, Norway, 24 April–1 May 1973," edited by T. Riste (Plenum, to be published).

[3] "Local Properties at Phase Transitions, Proceedings of the 'Enrico Fermi' Summer School, Varenna, 1973," edited by K. A. Müller and A. Rigamonti (Academic, to be published).

[4] T. Riste, E. J. Samuelsen, K. Otnes, and J. Feder, Solid State Commun. 9, 1455 (1971).

[5] S. M. Shapiro, J. D. Axe, G. Shirane, and T. Riste, Phys. Rev. B 6, 4332 (1972).

[6] J. K. Kjems, G. Shirane, K. A. Müller, and H. J. Scheel, Phys. Rev. B 8, 1119 (1973).

[7] F. Schwabl, Z. Phys. 254, 57 (1972), and Solid State Commun. 13, 181 (1973).

[8] For a survey see J. Feder, in "Local Properties at Phase Transitions, Proceedings of the 'Enrico Fermi' Summer School, Varenna, 1973," edited by K. A. Müller and A. Rigamonti (Academic, to be published).

[9] T. Schneider and E. Stoll, in "Local Properties at Phase Transitions, Proceedings of the 'Enrico Fermi' Summer School, Varenna, 1973," edited by K. A. Müller and A. Rigamonti (Academic, to be published).

[10] Th. van Waldkirch, K. A. Müller, and W. Berlinger, Phys. Rev. B 5, 4324 (1972).

[11] Th. van Waldkirch, K. A. Müller, and W. Berlinger, Phys. Rev. B 3, 1052 (1973).

[12] R. Kubo, in *Fluctuation, Resonance, and Relaxation in Magnetic Systems*, edited by D. ter Haar (Oliver and Boyd, London, 1972); G. Reiter, to be published.

[13] See K. A. Müller, in "Proceedings of the NATO Advanced Study Institute on Anharmonic Lattices, Structural Transitions and Melting, Geilo, Norway, 24 April–1 May 1973," edited by T. Riste (Plenum, to be published).

[14] A. Rigamonti, in "Local Properties at Phase Transitions, Proceedings of the 'Enrico Fermi' Summer School, Varenna, 1973," edited by K. A. Müller and A. Rigamonti (Academic, to be published).

[15] Th. van Waldkirch, thesis, University of Zurich, 1973 (unpublished).

[16] F. Borsa, in "Local Properties at Phase Transitions, Proceedings of the 'Enrico Fermi' Summer School, Varenna, 1973," edited by K. A. Müller and A. Rigamonti, (Academic, to be published), has most recently observed the critical slowing down in one-dimensional ferromagnets at several NMR frequencies.

[17] K. A. Müller, in "Local Properties at Phase Transitions, Proceedings of the 'Enrico Fermi' Summer School, Varenna, 1973," edited by K. A. Müller and A. Rigamonti (Academic, to be published).

[18] O. F. Schirmer and K. A. Müller, Phys. Rev. B 7, 2986 (1973).

[19] The constancy of the ratios $\Delta\omega/B^2$ is good except for $\theta = 45°$ which is a factor of 1.3 too high. The deviation becomes more pronounced for smaller B's and is not understood.

[20] W. G. Stirling, J. Phys. C: Proc. Phys. Soc., London 5, 2711 (1972).

Optical Kerr Effect, Susceptibility, and Order Parameter of Plastic Succinonitrile

T. Bischofberger and Eric Courtens*
IBM Research Laboratory Zurich, 8803 Rüschlikon, Switzerland
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The high-frequency electro-optic tensor of succinonitrile is measured throughout the plastic crystalline phase. Its strength, due to cooperative molecular response to the orienting optical field, is a generalized susceptibility increasing rapidly near the plastic-solid transition. Its anisotropy describes long-range cubic order of the average molecular orientation. This orientational order parameter decreases rapidly near the plastic-liquid transition, suggesting that the hitherto neglected average orientational order is essential to the plastic phase stability.

The plastic (P) phase of molecular crystals is characterized by continuous reorientation of molecules which form on the average a regular lattice.[1] It is a common intermediate phase between liquid (L) and solid (S) phases for "globular" molecules. Succinonitrile ($CN\text{-}CH_2\text{-}CH_2\text{-}CN$), though not strictly globular, exhibits an extended P phase melting at $T_M = 331.3°K$ and solidifying orientationally at $T_S = 233.3°K$.[2] The lattice is bcc in the P phase.[3] The molecules isomerize by rotation around the central C-C bond. The concentration of isomers is known[4] and their average position has recently been worked out.[5] A relatively strong depolarized Rayleigh wing has been measured[6] which suggests that the optically induced birefringence should also be large. The present Letter reports the measurement of the optical Kerr susceptibility $\overleftrightarrow{\chi}^{NL}$ on oriented