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Order-Disorder Behavior at Displacive Structural Phase Transitions

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We show that a suitable electron paramagnetic resonance experiment can discriminate sufficiently against the predominantly harmonic fluctuations characterizing a system undergoing a displacive phase transition, that a cluster-induced order-disorder component of the local behavior is exposed. We find evidence that, at T_c, the oxygen octahedra in $SrTiO_3$ oscillate about quasiequilibrium positions displaced by, typically, $\pm 0.22°$ from the high-symmetry site. This result provides quantitative understanding of the incomplete softening of the phonon mode.

In the last few years it has gradually come to be appreciated that the dynamical behavior of systems undergoing displacive structural phase transitions (dpt's) may differ in a qualitatively striking fashion from that suggested by the long-serving phenomenology of the "soft mode."[1] The recent activity may be traced to the observation[2] that the spectral function of the critical degrees of freedom in $SrTiO_3$ evolves, as $T \to T_c^+$, from the simple form expected for a softening quasiharmonic phonon, to a more complex form: A central peak appears and grows critically in intensity, while the phonon resonance continues to soften, but attains, at T_c, a finite limiting frequency $\omega_\infty^c = 0.13 \pm 0.02$ THz. While certain features of these results (notably the extremely narrow central-peak width[3]) are hard to understand without invoking extrinsic mechanisms,[4] the occurrence of similar effects in computer simulations,[5] and the apparently sample-independent character of ω_∞^c,[6] together leave little doubt that the behavior is, in part at least, intrinsic.

With the motivation of these observations there has emerged a new view[5,7,8] of the physics of dpt's: With the onset of criticality, the growth in correlations drives a crossover from a weakly anharmonic ("displacive") regime to a strongly anharmonic ("order-disorder") regime, whose short-range order is manifested in clusters, in which the average value of the ordering variable ("cluster coordinate") is nonzero for a time long[9] in comparison with typical inverse phonon frequencies. The central peak may thus be regarded as the short-range-order-induced dyanmic precursor of the Bragg peak to appear below T_c, while the phonon sideband reflects quasiharmonic oscillations about the distorted quasiequilibrium positions set by the distribution of cluster coordinates. The essential nonlinearities of the critical region enter through the nonlinear dynamics of the cluster coordinates, which introduces into the local behavior the anharmonic features of an order-disorder system.

While this picture is conceptually appealing, it is without the foundation of analytic theory and, until now, has also lacked direct experimental support. In this Letter, we show the following:

(i) In a static structure determination, the predicted order-disorder character of the dpt will be masked by the quasiharmonic fluctuations; however, a suitable EPR experiment can, through motional narrowing, discriminate sufficiently against these fluctuations that the nonlinear character of the local behavior is exposed.

(ii) This situation is, in fact, realized in EPR experiments on monodomain-transforming $SrTiO_3$,[10] where motional narrowing suppresses the contribution of the quasiharmonic fluctuations by a factor $\sim 10^2$.

(iii) The anharmonic local behavior, thus exposed, suggests a degree of precursor order (at T_c) which accounts remarkably well for the observed limiting value, ω_∞^c, of the soft-mode frequency.

Motivated by the cluster picture, we suppose that the time-dependent local scalar coordinate $x(t)$, whose ensemble average is the order parameter for the dpt, can be written in the form[7a]

$$x(t) = \sigma(t) + y(t). \quad (1)$$

Here the coordinate $y(t)$ is taken to be a Gaussian random variable, with correlation time τ_y, and mean-square amplitude $\langle y^2\rangle$: This variable describes the quasiharmonic fluctuations about the instantaneous quasiequilibrium position set by the value of the coordinate $\sigma(t)$, which reflects the influence of the clusters. The simplest variant (s.v.)[7a] of the cluster picture suggests that the coordinate σ be taken to undergo Markovian hopping between *two* values, $\pm\sigma_0$, with a transition probability per unit time $1/\tau_\sigma$, where $\tau_\sigma \gg \tau_y$. This is clearly an oversimplification: The large thickness of cluster walls in displacive systems[7b] demands a more refined variant (r.v.) of the cluster picture, allowing for a continuous *distribution*, $P(\sigma)$, of quasiequilibrium positions —a distribution which one would expect to display a strongly anharmonic (possibly double-peaked) structure.

Within this picture it is immediately clear that the nonlinear features of the local behavior will be revealed in the *equilibrium* probability distribution function (pdf) $P_0(x)$ *only* if the spread in quasiequilibrium positions is comparable with the amplitude of the harmonic motion: In s.v., the pdf will consist of two Gaussians, centered on $\pm\sigma_0$ and of variance $\langle y^2\rangle$, which can be "resolved" only if $\sigma_0^2 > \langle y^2\rangle$. Our estimates (below) for $SrTiO_3$ suggest that this condition will not be fulfilled near any phase transition remotely describable as "displacive."[11] Thus x-ray and neutron-scattering structural investigations which determine the pdf through its Fourier transform (the Debye-Waller factor) cannot in general be expected to detect the cluster-induced nonlinear local behavior.

Consider now, however, the spectral density determined by an EPR probe, chosen such that the instantaneous shift ω in Larmor frequency depends linearly upon the local coordinate: $\omega = Bx$. The resonance absorption is then determined by the function[12]

$$I(\omega) = \int_0^\infty e^{-i\omega t}\langle \exp[iB\int_0^t x(t')dt']\rangle dt + \text{c.c.} \qquad (2)$$

In the limit in which the time evolution of both the coordinates y and σ is slow on the time scale of the EPR probe (the inverse of the EPR linewidth[12]) it is easily seen that $I(\omega) \approx P_0(\omega/B)$ so that the line shape mirrors the equilibrium pdf. In general, however, the quasiharmonic fluctuations will be sufficiently fast that their contribution to the linewidth will be motionally narrowed, with consequences that are again most explicitly revealed within s.v.: A straightforward calculation shows that, provided $r \equiv \sigma_0^2\tau_\sigma/\langle y^2\rangle\tau_y \gg 1$, there will exist a *range* of values of the sensitivity parameter B, with upper and lower limits $B_U \sim \sigma_0/\langle y^2\rangle\tau_y$, $B_L \sim 1/\sigma_0\tau_\sigma$, between which the double-sited character of the local dynamics (envisaged in s.v.) will be revealed in a correspondingly double-peaked structure in $I(\omega)$; the window between B_U and B_L becomes smaller with r, vanishing at a value of r of order unity. Within the window the EPR probe is slow enough to discriminate effectively against the fast quasiharmonic fluctuations but not so slow that the double-peaked form of $I(\omega)$ is erased by the intersite hopping. More generally, in r.v., provided the time scales of the σ and y coordinates are sufficiently well separated, there will exist a window where the discrimination against the harmonic fluctuations is sufficient that $I(\omega) \approx P(\sigma/B)$: This is precisely the situation encountered in the ($T \approx T_c$) EPR measurements on monodomain $SrTiO_3$,[13] to which we now turn.

In the noncritical region the 19.2-GHz (3080 G) resonance at the Fe^{3+} V_0 center (for which $B \approx 1.6 \times 10^8$ Hz/deg with $H \parallel [110]$) is characterized by a near-Lorentzian line, whose half-width, with estimated background contributions subtracted,[14] is $\Gamma \approx 1.5 \times 10^6$ Hz at 130 K. With the approach to T_c the line shape evolves from Lorentzian, through Gaussian, to the "over-Gaussian" form[13] displayed in Fig. 1(a); simultaneously the line broadens, attaining a maximum half-width (close to T_c) of $\Gamma \approx 5 \times 10^7$ Hz. Recent measurements[14] have established that, in the region $T_c < T < 117$ K, the observed linewidth scales linearly with the sensitivity parameter B, showing that the line shape determines a distribution of distortions that evolve slowly on the scale of the EPR experiment.

In analyzing these results we first establish the crucial importance of motional narrowing. High-resolution structural studies[15] of $SrTiO_3$ yield[16] $\langle y^2\rangle \approx 4.4°$ (Ref. 2) at $T_c + 10$ K. In the absence of motional narrowing these fluctuations would make a contribution to the EPR line half-width $\approx \langle y^2\rangle^{1/2}B \approx 3.3 \times 10^8$ Hz, altogether masking the nonlinear local behavior. The simple motional-narrowing theory[12] shows that, in fact, the half-width contribution made by these fluctuations will be reduced to $B^2\langle y^2\rangle\tau_y$; since τ_y should be at most $\sim 10^{-11}$ sec,[17] this contribution will be no more than $\sim 10^6$ Hz, *small* in comparison with the observed half-width close to T_c, and comparable with the observed half-width in the noncritical region (noted above), where the quasiharmonic fluctuations should indeed be dominant.

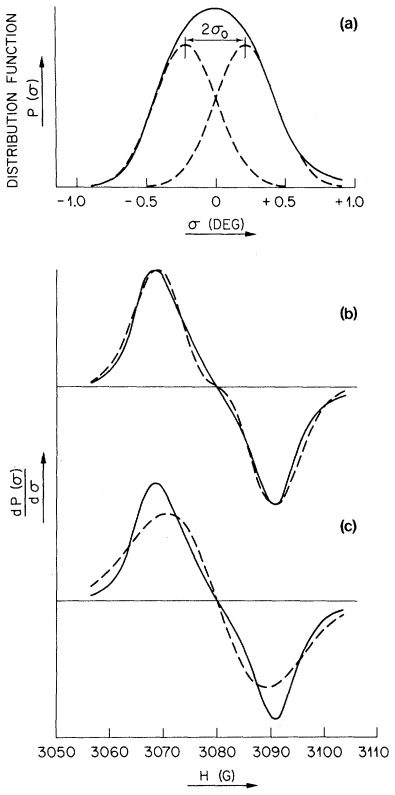

FIG. 1. (a) The experimental distribution function $P(\sigma)$ at $T = 105.5$ K (solid line) together with two displaced Gaussians with whose superposition (not shown) we model the spectrum. The high-field tail reflects a small dispersive part in the EPR signal. (b) The derivative of the experimental $P(\sigma)$ (solid line), and of its double-Gaussian representation defined in (a). (c) The derivative of $P(\sigma)$ and its single-Gaussian representation.

We now turn to discuss the distribution function $P(\sigma)$ itself. A comparison of the *derivative* of this function (acutally the quantity measured by the EPR experiment) with that of a Gaussian of the same peak height clearly reveals the non-Gaussian nature of $P(\sigma)$ [Fig. 1(c)]. The extent of its anharmonic character is objectively and illuminatingly characterized by its representation as a superposition of two symmetrically displaced Gaussians [Fig. 1(a)], whose separation provides one adjustable parameter, which we have chosen so as to optimize the corresponding representation of the derivative spectrum [Fig. 1(b)].

These results establish, unambiguously, the existence of local precursor order persisting for times long in comparison with 10^{-8} sec. More explicitly, Fig. 1 suggests that, near but above $T_c = 105.3$ K,[18] the oxygen octahedra in $SrTiO_3$ oscillate typically about quasiequilibrium positions displaced by $\sigma_0 \approx 0.22°$ from the high-symmetry position.[19] We now show, finally, that, when interpreted within the cluster picture, this result affords a natural interpretation of the behavior of the soft-phonon side band. According to the cluster picture, the local order revealed by these results will exhibit spatial coherence over a volume of the order of a cluster size: It follows that the frequency of the softening high-temperature phonon (for which the local order is effectively static) will not vanish at T_c, but will be stabilized by the short-range order, in much the same way as the low-temperature phase phonon is stabilized by the true long-range order. According to Raman-scattering experiments,[20] below T_c the A_{1g} soft-phonon frequency grows with the order parameter at a rate of 0.69 THz/angular degree: Thus we estimate that, close to T_c, the soft phonon will attain a limiting frequency $\omega_\infty^c \approx 0.69\sigma_0 \approx 0.15$ THz. The striking accord with the experimental value cited above constitutes, we believe, strong evidence for the overall coherence of the picture we have described.[21]

In summary, we have shown that an EPR probe can selectively expose the local nonlinear effects, anticipated at dpt's but masked in other measurements by a large harmonic phonon background. In particular we have shown that EPR measurements on $SrTiO_3$ do indeed offer evidence of a nonlinear, "order-disorder," local behavior, driven by the formation of long-lived clusters of precursor order.

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[16]In monodomain $SrTiO_3$ the ordering variable x is an *angular* coordinate describing the rotation of an oxygen octahedron about the monodomain axis: Our estimate of $\langle y^2 \rangle$ presupposes that the rotational degrees of freedom make the dominant contribution to the mean-square *displacement* of oxygen ions in the Sr-O plane.

[17]The order of the inverse saturation frequency of the soft mode.

[18]We base this estimate on EPR experiments showing that the fluctuations about axes *perpendicular* to the monodomain axis peak at 105.3 ± 0.2 K. Within Landau theory, this temperature is identical with T_c; a fluctuation-corrected theory suggests that this temperature actually represents an upper bound on T_c.

[19]Mindful of the uncertainties in T_c we emphasize that this degree of *local* order cannot reasonably be attributed to true *long-range* order: Were σ_0 merely a measure of the (long-range) order parameter, it would decrease steeply with temperature (vanishing within ~ 0.1 K), producing a decrease in the linewidth much steeper than that observed.

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Anomalous Specific Heat of a One-Dimensional Disordered Solid

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We show the existence of localized low-energy excitations of configurational nature in a one-dimensional model of a disordered solid. The corresponding extra specific heat is computed and its relation to glasses and superionic conductors is discussed.

The long-standing problem of the low-temperature extra specific heat of glasses and amorphous materials[1] receives further interest from the recent measurements of analogous effects on superconducting disordered metals[2] and on various β-alumina compounds.[3] These observations confirm the hypothesis that the extra specific heat is due to intrinsic properties of the disordered state.

The phenomenological model that seems to be the most consistent with respect to specific heat and other properties[1] is based on the assumption that two-level systems exist in disordered systems and that the occurrence probability of various energy gaps is constant for small gaps.[4]

Here we consider a model Hamiltonian that describes a one-dimensional disordered solid and we explicitly compute the configurational density of states. The existence of low-energy excitations of configurational type is established for a wide range of the parameters and estimations are made for the occurrence probability of various energy gaps.

The model we study is the Frenkel-Kontorowa one-dimensional dislocation model[5] with a finite density of defects [$\rho_p \neq 1$ in Eq. (3)]. We remark that for a finite density of defects it is not possible to describe the system in terms of a simple sine-Gordon field equation and also a defect cannot be simply identified with a soliton. This is possible only in the dilute case.[6] The interpretation of this model in terms of superionic conduc-