

Sound propagation in ammonium halides near the tricritical point

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The dynamic behavior of the acoustic response near the tricritical point in an elastically isotropic Ising system has been studied above T_c . The tricritical exponents and the corresponding scaling functions for the sound attenuation and dispersion are given in two limiting regimes. An explanation of the measured sound-attenuation exponents in ammonium halide crystals is proposed.

It is known^{1,2} that, if a system of Ising spins is coupled to an isotropic elastic medium, a first-order transition is expected to take place under constant pressure. However, the discontinuity of the order parameter (OP) is usually small, so the change in the critical behavior is observed only extremely close to the transition temperature. This kind of behavior, known as pseudocritical,² is characterized by rigid Ising-model exponents. Recently the role of finite elastic coupling in the critical sound propagation in Ising systems was also investigated.³ It was shown that, within the pseudocritical region, a crossover is expected from the conventional “weak-coupling” regime to the “strong-coupling” regime where the lowest order in the elastic coupling approximation is inapplicable. Since the magnitude of these effects is determined by the value of the specific-heat exponent, which is rather small ($\alpha_{\text{Ising}} \approx 0.1$), we expect that these effects might best be observed near the Gaussian pseudotricritical point ($\alpha=0.5$ in three dimensions) which, as is expected, may also occur in compressible Ising systems.^{2,4} Such a pseudotricritical point would separate a line of weakly first-order transitions from a line of points with distinct first-order discontinuities. The multicritical points observed in ammonium halide crystals, undergoing order-disorder structural transitions, presumably are pseudotricritical points of this type.^{2,5} Experimental studies on sound propagation near tricritical points in these crystals⁶ have revealed that the measured tricritical sound attenuation exponents are considerably lower than the conventional value obtained from molecular-field (Gaussian) theory in the limit of small compressibility.⁷ The purpose of this paper is to demonstrate that these data can be understood in terms of the theory suitable for the regime of strong spin-lattice coupling.

To describe the spin system coupled to an isotropic elastic medium we consider the following Hamiltonian:

$$H = \frac{1}{2} \int d^d x \left[r_0 S^2 + (\nabla S)^2 + \frac{1}{2} \tilde{u}_0 S^4 + C_{12}^0 \left(\sum_{\alpha} e_{\alpha\alpha} \right)^2 + 2C_{44}^0 \sum_{\alpha,\beta} e_{\alpha,\beta}^2 + 2g_0 \sum_{\alpha} e_{\alpha\alpha} S^2 + 2p \sum_{\alpha} e_{\alpha\alpha} \right], \quad (1)$$

where the OP is denoted by $S(x)$ and $e_{\alpha\beta}(x)$ are com-

ponents of the strain tensor. The symbols $C_{\alpha\beta}^0$ stand for the bare elastic constants and g_0 is the bare coupling constant. The last term describes the effect of external pressure p .

Following Larkin and Pikin⁸ we decompose the elastic configuration into a homogenous deformation and a phonon part

$$e_{\alpha\beta} = e_{\alpha\beta}^0 + \frac{1}{2} i V^{-1/2} \sum_{\mathbf{k},\lambda} [k_{\beta} e_{\alpha}(\mathbf{k},\lambda) + k_{\alpha} e_{\beta}(\mathbf{k},\lambda)] \times Q_{\mathbf{k},\lambda} \exp(i\mathbf{k} \cdot \mathbf{x}), \quad (2)$$

where $Q_{\mathbf{k},\lambda}$ is the normal coordinate, $\mathbf{e}(\mathbf{k},\lambda)$ is the polarization vector, and V is the volume of the system. The mass density was assumed to be equal to one. Next, we integrate over the homogenous deformations and get, in result, a shift of the transition temperature and a long-ranged, strain-mediated interaction term

$$- \frac{w_0}{4V} \left[\int d^d x S^2(x) \right] \left[\int d^d y S^2(y) \right] \quad (3)$$

in a new Hamiltonian denoted, henceforth, by \bar{H} , with $w_0 = 2g_0^2/B^0$ and

$$B^0 = C_{11}^0 - \frac{2(d-1)}{d} C_{44}^0$$

being the bulk modulus.

The dynamics of the system is described by the coupled Langevin equations for the OP field and the acoustic phonons,⁹ which, in the path-integral formalism,¹⁰ are equivalent to the Lagrangian

$$L = \sum_{\mathbf{k}} \int dt \left[\tilde{S}_{\mathbf{k}} \Gamma_0 \tilde{S}_{-\mathbf{k}} - \tilde{S}_{\mathbf{k}} \left[\dot{S}_{-\mathbf{k}} + \Gamma_0 \frac{\partial \bar{H}}{\partial S_{-\mathbf{k}}} \right] + \frac{1}{2} \Gamma_0 \frac{\partial^2 \bar{H}}{\partial S_{\mathbf{k}} \partial S_{-\mathbf{k}}} + \sum_{\lambda} \tilde{Q}_{\mathbf{k},\lambda} Dk^2 \tilde{Q}_{-\mathbf{k},\lambda} - \tilde{Q}_{\mathbf{k},\lambda} \left[\ddot{Q}_{\mathbf{k},\lambda} + \frac{\partial \bar{H}}{\partial Q_{-\mathbf{k},\lambda}} + Dk^2 \dot{Q}_{-\mathbf{k},\lambda} \right] \right], \quad (4)$$

where $\tilde{S}_{\mathbf{k}}$ and $\tilde{Q}_{\mathbf{k},\lambda}$ are the auxiliary response fields.

The quantity of interest is the acoustic self-energy for the longitudinal phonons (the transversal modes are not

coupled with the OP in our model), which can be expressed through the energy-response function $C(k, \omega)$ in the form^{3,11}

$$\Sigma(k, \omega) = \frac{2g_0^2 k^2 C(k, \omega)}{1 + v_0^{\text{ph}} C(k, \omega)}, \quad (5)$$

where $v_0^{\text{ph}} = 2g_0^2 / C_{11}^0$ and

$$C(k, \omega) = \langle \Gamma_0 (\bar{S}S)_{\mathbf{k}, \omega} (S^2)_{-\mathbf{k}, -\omega} \rangle_{L_{\text{OP}}^{\text{eff}}}. \quad (6)$$

The average in Eq. (6) is calculated with the effective OP Lagrangian $L_{\text{OP}}^{\text{eff}}$ containing the usual (local) four-spin interactions with the renormalized coupling constant $u_0 = \bar{u}_0 - v_0^{\text{ph}}$ as well as the strain-mediated (nonlocal) interactions with the coupling constant $v_0 = 2g_0^2(1/B^0 - 1/C_{11}^0)$. The other effective OP interactions generated in $L_{\text{OP}}^{\text{eff}}$ are strongly irrelevant¹² and have been left out as they do not contribute to the leading tricritical behavior. The second term in the denominator of Eq. (5), usually omitted in the lowest order in spin-phonon coupling theories, turns out to be of crucial importance for the systems with large positive specific-heat exponent and strong coupling between the OP and the acoustic phonons.

The coupling v_0^{ph} would become temperature dependent if we wrote the factor $k_B T$ incorporated in the elastic constants in (1) in the explicit form. Thus, the relative magnitude of both terms in the effective coupling constant $u_0 = \bar{u}_0 - v_0^{\text{ph}}$ depends strongly on temperature. Since the transition temperature is pressure dependent, u_0 can change its sign somewhere on the line $T_c(p)$. Also, higher-order couplings (like $\sum_{\alpha} e_{\alpha\alpha} S^4$) may bring about a similar effect.^{2,13} According to the hypothesis of Riedel and Wegner,¹⁴ the tricritical behavior related to the change of sign of the four-spin coupling constant is determined by the Gaussian fixed point with $\alpha = \varepsilon/2$ ($\varepsilon = 4 - d$). In a compressible system, this fixed point is additionally unstable against perturbations along v but, as was argued by Sak,¹ the rigid fixed point can control the behavior of the system over a wide interval of temperatures provided that v_0 is sufficiently small.

On the grounds of Eq. (5), we have found two distinct pseudotricritical regimes of the acoustic behavior depending on the relative size of the reduced temperature $t = (T - T_c)/T_c$, frequency ω , and the parameter $a = v_0^{\text{ph}} / v^*$, where $v^* = \varepsilon / K_d$ with

$$K_d^{-1} = 2^{d-1} \pi^{d/2} \Gamma(d/2).$$

In the weak-coupling regime,³ $a \rightarrow 0$ or, for $t^2 + (\omega/2\Gamma_0)^2 > a^4$, the phenomenological theory relations⁷ for the sound attenuation coefficient and dispersion are recovered ($d=3$)

$$\begin{aligned} \alpha(\omega, t) &\sim t^{-\rho_A} \omega^2 g_A(y), \\ c^2(\omega, t) - c^2(0, t) &\sim t^{-1/2} f_A(y), \end{aligned} \quad (7)$$

where $\rho_A = z\nu + \alpha$, $y = \omega t^{-z\nu} / \Gamma_0$,

$$g_A(y) = 32y^{-2} \text{Re}[D(y)],$$

and

$$f_A(y) = 4y^{-1} \text{Im}[D(y)] + 1$$

with

$$D(y) = (1 - iy/2)^{1/2} - 1.$$

For the relaxational dynamics, the dynamic tricritical exponent $z=2$, thus, one finds $\rho_A = 1.5$. In this regime, the sound can be treated as an infinitesimal perturbation acting on the OP system. However, for $C_{44}^0 \ll C_{11}^0$ (i.e., for small v_0), there is another tricritical regime corresponding to $a \rightarrow 1$ or $t^2 + (\omega/2\Gamma_0)^2 < a^4$. In this strong-coupling regime, qualitatively different behavior can be observed described by

$$\begin{aligned} \alpha(\omega, t) &\sim t^{-\rho_B} \omega^2 g_B(y), \\ c^2(\omega, t) - c^2(0, t) &\sim t^{1/2} f_B(y), \end{aligned} \quad (8)$$

where $\rho_B = z\nu + \alpha/2$,

$$g_B(y) = 16y^{-3/2} \text{Re}[D(y)^{-1}] \{ \text{Im}[D(y)^{-1}] \}^{-3/2},$$

and

$$f_B(y) = \frac{1}{2} y \text{Im}[D(y)^{-1}] - 2.$$

This strong-coupling limit is analogous to the liquid critical point.¹⁵

One may suppose that a rather large difference between ρ_A and ρ_B could be distinguished experimentally. Ammonium halides like NH_4Cl and NH_4Br are examples of the systems which, at high pressures, can be described in terms of the compressible Ising model with considerable spin-lattice coupling^{6,16} and, in this case, the results of our theory can be applied. Measurements of the sound-attenuation coefficient in the hydrodynamic region ($y \ll 1$) near the tricritical point gave the values $\rho = 1.20 \pm 0.05$ for NH_4Br and $\rho \approx 1.2 - 1.1$ for NH_4Cl .⁶ These results correspond quite well with the strong-coupling regime exponent $\rho_B = 1.25$ and differs significantly from the value $\rho_A = 1.5$, which suggests that the weak-coupling approximation is inapplicable to these crystals. A slightly lower value of the tricritical sound-attenuation exponent $\rho = 1.1 \pm 0.1$ found for ND_4Cl (Ref. 6) seems to be a result of decreasing of the effective correlation length exponent, due to the long-ranged interactions, as the region of the first-order transition is approached.³

The reduced temperature $t_{\text{cross}} \approx a^2$, at which the cross-over from a weak-coupling to a strong-coupling regime takes place [i.e., the term $v_0^{\text{ph}} C(k, \omega)$ dominates in the denominator of Eq. (5)], can be estimated from sound-attenuation measurements. Equations (7) and (8) in the hydrodynamic region get reduced to the form

$$\alpha = (\pi \tau_0 a / 64 c_0) \omega^2 t^{-\rho_A} \quad (7')$$

for the weak-coupling regime and

$$\alpha = (\pi^{1/2} \tau_0 a^{1/2} / 32 c_0) \omega^2 t^{-\rho_B} \quad (8')$$

for the strong-coupling regime, with c_0 being the bare longitudinal velocity and $\tau_0 = 1/\Gamma_0$ the bare relaxation time. Here the nonuniversal proportionality factors are

written explicitly. The ultrasonic attenuation data in Ref. 6 were fitted to the single relaxation function. In the hydrodynamic region, where most of the measurements were performed, this function gets reduced to the form

$$\alpha = \bar{C}\omega^2\tau', \quad (9)$$

where \bar{C} is a relaxation strength and $\tau' = \tau'_0 t^{-\rho}$ is an acoustic relaxation time which incorporates the total temperature dependence of the attenuation coefficient in the hydrodynamic region. Comparing the nonuniversal amplitudes of Eqs. (7') and (9), we obtain $a = 64\bar{C}c_0\eta/\pi$, where the correction factor $\eta = \tau'_0/\tau_0$ has been introduced to account for the ratio of the bare relaxation times. The simplest assumption is that $\eta = 1$. Taking the value of \bar{C} from Ref. 6, we would find that the crossover temperature was equal to 6×10^{-2} for NH_4Br and 0.2 for ND_4Cl (for NH_4Cl it was not possible to determine the value of \bar{C})⁶ if the measurements were carried out in the weak-coupling regime. If we compare Eqs. (8') and (9), we find that $a = (32\bar{C}c_0\eta/\pi)^2$, hence $t_{\text{cross}} \simeq 2 \times 10^{-3}$ for NH_4Br and $t_{\text{cross}} \simeq 3 \times 10^{-2}$ for ND_4Cl .

The crossover temperature can also be estimated for ND_4Cl from the measurements of thermal expansion¹⁷ and from the pressure dependence of transition temperature ($\partial T_c/\partial p$ can be obtained from Table II in Ref. 6). The value $t_{\text{cross}} \simeq 5 \times 10^{-2}$ obtained in this way is in qualitative agreement with that obtained above. As the sound-attenuation exponent for ammonium halides was determined in the range $9 \times 10^{-4} < t < 4 \times 10^{-2}$, thus the weak-coupling regime can be ruled out for ND_4Cl .

The situation for NH_4Br is less convincing as the value 2×10^{-3} lies well inside the experimental temperature range. However, it is worth mentioning that the theoretical temperature limit t_{cross} for the strong-coupling regime is very sensitive to the ratio $\eta = \tau'_0/\tau_0$ and therefore a slightly higher (than unity) value of η for NH_4Br would prove that the measurements really refer to the strong-coupling regime. Hence, some independent measurements of tricritical bare relaxation time τ_0 for these crystals, as well as further ultrasonic measurements covering the range $\omega\tau > 1$, would be highly desirable.

The crossover temperature of an order of a few hun-

dreds also seems to be consistent with the character of the curves in Figs. 2 and 3 in Ref. 6, where the tricritical temperature dependences of τ' [which reflects the temperature dependence of $\alpha(\omega, t)$ in the hydrodynamic region] for NH_4Br and ND_4Cl are displayed. Below $t_c \simeq (2-5) \times 10^{-2}$, a change in the power-law behavior can be observed. The slope of the curves changes from the value $\rho \simeq 1.1-1.2$ for $t < t_c$ to a much higher value $\rho \simeq 1.5$ when $t > t_c$. However, as the data for $t > t_c$ are considerably scattered, the power-law behavior in this temperature range is not sufficiently established.

At this point we should note that the assumption that the first-order jump [proportional to $(v_0/u_6)^{1/2}$ in the mean-field theory, where u_6 is the coupling constant of the sixth-order term in the free energy] is small and the metastability region (proportional to v_0^2/u_6 in the mean-field theory) also depends on weak OP coupling. However, hysteresis can still be small if u_6 is sufficiently large as it seems to occur in ammonium halides where very little indication of any hysteresis in tricritical heat-capacity measurements has been reported.⁴ In the case of NH_4Cl at 1500 bar and ND_4Cl at 1 atm hysteresis less than 10 and 30 mK, respectively, was observed. The corresponding reduced temperature is about 1×10^{-4} so the region where the first-order character is pronounced lies well outside the temperature range where the ultrasonic measurements were carried out.

In a more detailed analysis of the problem of tricritical sound propagation in these crystals, the effects of long-ranged interactions, elastic anisotropy, as well as scaling fields describing the crossover to the critical behavior should be taken into regard. Also, the difference between adiabatic and isothermal velocity may contribute to such an analysis.

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