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Dynamic critical phenomena in ammonium halide crystals

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All available ultrasonic and hypersonic data on NH_4Br, NH_4Cl, and ND_4Cl have been analyzed over a wide range of temperature, pressure, and frequency in the disordered cubic phase D, the "ferro-ordered" cubic phase O_c, and the "antiferro-ordered" tetragonal phase O_T. The acoustical absorption and dispersion in the disordered phase can be interpreted in terms of a single relaxation time τ that exhibits critical behavior $\tau \sim \Delta T^{-\theta}$ near the order-disorder transition. The resulting values of the critical exponents θ confirm the existence of a master phase diagram for these systems. In the tetragonal regime (NH_4Br at 1 atm) the experimental value $\theta = 1.38$ for $T > T_c$ corresponds quite well with the critical exponent $z\nu$, describing order-parameter relaxation for $n = 3$ fixed points in Hohenberg and Halperin's model A. In the D-O_c-O_T triple-point regime (NH_4Cl at 1 atm, NH_4Br at 1.88 kbar) the experimental value $\theta = 1.0$ corresponds to $z\nu$ given by conventional theory, which is appropriate for model A near higher-order critical points. In the multicritical regime (ND_4Cl at 1 atm, NH_4Cl at 1.5 kbar, NH_4Br at 3.25 kbar) the experimental values of θ (1.1 to 1.2) associated with this D-O_c multicritical point cannot be easily interpreted in terms of currently available theory. The critical relaxation times were obtained using acoustical relaxation strengths that are independent of temperature, and several pieces of experimental evidence are presented in support of this method of analysis.

I. INTRODUCTION

Order-disorder transitions in ammonium-halide crystals have been studied extensively, and it now appears that cooperative phenomena in NH_4Cl, ND_4Cl, NH_4Br, and ND_4Br can be correlated in terms of the master phase diagram shown in Fig. 1.[1,2] At high temperatures (up to ~400 K), all these salts have a disordered $Pm3m$ cubic structure D with the tetrahedral NH_4^+ ions randomly distributed between two equivalent orientations. Two kinds of ordered phase are observed: a $P\bar{4}3m$ cubic structure O_c which is "ferro ordered", and a $P4/nmm$ tetragonal structure O_T which is "antiferro ordered".[1] Two important features of the master phase diagram are the D-O_c-O_T triple point and a multicritical point along the D-O_c transition line. The triple point is closely analogous to the tetracritical and bicritical points that occur in antiferromagnetic spin-flop systems. The multicritical point (p^*, T^*) indicates the boundary between weakly first-order D-O_c transitions for $p < p^*$ and continuous transitions for $p \geq p^*$.[2] This point has been compared to a tricritical point in magnetic systems, but the critical exponent β seems to indicate a higher-order critical point.[3,4]

We are concerned here with the dynamical aspects of critical phenomena in ammonium halides, but it is appropriate to comment briefly on the current status

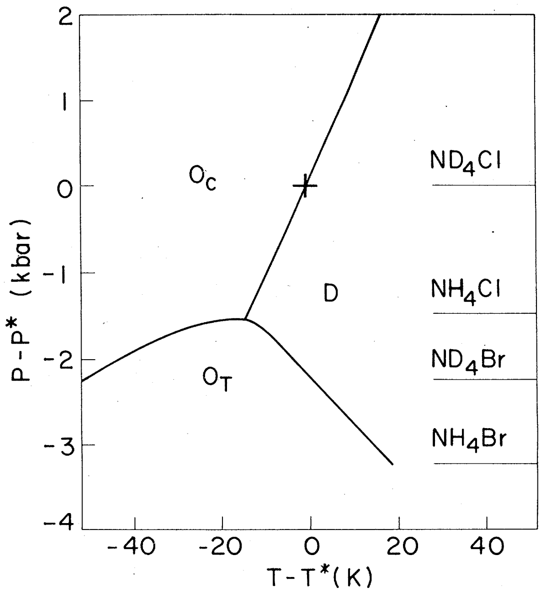

FIG. 1. Master phase diagram for ammonium chloride and bromide. The D-O_c multicritical point p^*,T^* (indicated by + symbol) is at 3.2 kbar, 215.8 K for NH_4Br; 2.2 kbar, 215 K for ND_4Br; 1.5 kbar, 256 K for NH_4Cl; 1 bar, 249.4 K for ND_4Cl. The location of $p = 0$ is indicated on the left for each salt.

of theoretical models for the static properties. The behavior of ammonium chloride has frequently been discussed in terms of compressible Ising models in which there is coupling between the acoustic phonons and a single Ising-like pseudospin order parameter.[5] However, it has been shown recently that this model is not consistent with the behavior of the elastic and thermal properties of NH_4Cl and ND_4Cl.[6] The presence of antiferro ordering in ammonium bromide can be rationalized in terms of two theoretical models[7,8] involving competing interactions—a direct interaction that favors ferro ordering and an indirect interaction that favors antiferro ordering. However, neither of these models adequately explains the effect of deuteration.[1] The best of the available models seems to be that of Yamada *et al.*,[8] but a better treatment of the coupling to acoustic phonons and the possible addition of coupling between ammonium-ion orientations and librational motions appears to be needed.

A wide variety of experimental information is available about the dynamical response of ammonium-halide crystals near their order-disorder transitions. These studies include acoustic measurements in the ultrasonic[2,6,9–22] and hypersonic[23–27] range, NMR measurements of the proton spin-lattice relaxation times,[28–33] a few NMR measurements of the quadrupole spin-lattice relaxation of the halide nuclei,[34–36] and several neutron investigations.[37–39] The numerous ultrasonic, Brillouin-scattering, and proton-NMR references are summarized in Table I for convenience.

The objective of this paper is to present a coherent analysis of all available ultrasonic and hypersonic absorption and dispersion data on NH_4Br, NH_4Cl, and ND_4Cl. This analysis will be carried out in terms of current theoretical models for the critical behavior of acoustic properties.[40–43] The principal result of such an analysis is the determination of the temperature dependence of the acoustic relaxation time τ on approaching various transition points. These acoustic τ values (which diverge on approaching the transition) will be compared with NMR correlation times (which do not). More importantly, the acoustic relaxation rate $1/\tau$ should provide a measure of the critical rate of order-parameter relaxation, which will be discussed in terms of recent theoretical models for dynamic critical phenomena.[44,45]

TABLE I. References to ultrasonic, hypersonic (Brillouin scattering), and proton NMR studies of ammonium halides.

System, pressure	Ultrasonic	Hypersonic	NMR
NH_4Br, 1 atm	2,9,11,17,18,21	26	29,33
NH_4Cl, 1 atm	10,12–14,18–20	23–25	28,30–32
ND_4Cl, 1 atm	22		30
NH_4Br, high press.	2,11,15		33
NH_4Cl, high press.	12,16,18,19	27	32
ND_4Cl, high press.	6		

II. PRESENTATION OF RESULTS

A. Theoretical framework

The theory of acoustic absorption and dispersion due to critical fluctuations of the order parameter has been studied extensively by Kawasaki.[40] The Kawasaki model most pertinent to the present systems is a magnetic solid with volume-magnetostrictive (i.e., "quadratic") coupling between the strain and the order parameter. Other authors[41–43] have discussed acoustic models involving structural phase transitions and n-component order parameters with more complicated coupling schemes. In particular, Matsushita[43] has developed a theory for the acoustic properties of ammonium halides by applying mode-coupling procedures to the pseudospin-phonon coupled mode of Yamada *et al.*[8] In this model there is an effective Ising "exchange integral" $J^{\text{eff}} \equiv J^d + J^{\text{ind}}$ made up of a direct octupole-octupole interaction between nearest-neighbor NH_4^+ ions and an indirect interaction involving a bilinear coupling of pseudospins with lattice phonons having wave vectors $\vec{k} \neq 0$. A sound wave of wave vector $\vec{q}$ is coupled to the order parameter via strain modulation of the effective exchange integral (a symmetry-allowed term linear in strain and quadratic in a pseudospin variable that is identical to volume-magnetostrictive-type coupling). We will cite the results of both Kawasaki and Matsushita. In the former case, quite general conclusions are obtained about the dynamical behavior of simple models; in the latter case, detailed predictions are made about the role of direct and indirect coupling in ammonium-halide crystals.

The critical behavior of an acoustic wave of frequency $\omega = 2\pi f$, wave vector $\vec{q}$, and polarization μ can be described in terms of a complex frequency-dependent amplitude-attenuation coefficient $\hat{\alpha}_{\vec{q}\mu}(\omega)$. The absorption α and dispersion D are then given by

$$\frac{\alpha}{\omega} = \frac{1}{\omega}\,\mathrm{Re}\,\hat{\alpha}; \quad D \equiv \frac{u^2(\omega) - u^2(0)}{2u(\omega)u^2(0)} = -\frac{1}{\omega}\,\mathrm{Im}\,\hat{\alpha} \ , \tag{1}$$

where $u(\omega)$ is the velocity at frequency ω and $u(0)$ is the static adiabatic velocity. Although there could be several slow variables making a contribution to $\hat{\alpha}$, it is likely that the dominant contribution in the disordered phase will arise from coupling to two order-parameter fluctuations. In this case, the complex attenuation has the form[40,43]

$$\frac{\hat{\alpha}}{\omega} = C\hat{F}(\omega\tau) \ , \qquad (2)$$

where $\tau = 1/2\Gamma_\xi$, and Γ_ξ is the characteristic relaxation rate for order-parameter fluctuations. From dynamic scaling one obtains[44]

$$\tau = \xi^z f(\vec{k}\,\xi) = \tau_0 t^{-z\nu} \ , \qquad (3)$$

where the scaling function $f(\vec{k}\,\xi)$ is evaluated at $\vec{k}\,\xi = 1$ and is independent of the reduced temperature $t \equiv |\Delta T|/T_c$, z is the dynamic critical exponent, and ν is the critical exponent associated with the static correlation length ξ.

Our aim is to characterize the behavior of the experimentally observed quantities α/ω and D as functions of $\omega\tau$ and to analyze the resulting τ values in terms of Eq. (3) and various theoretical predictions for $z\nu$. In order to proceed, it is necessary to be more specific about the nature of the relaxation strength C and the complex relaxation function $\hat{F}$.

In Matsushita's model,[43] the relaxation strength is given by

$$C = a\,|L(\vec{k}_{\mathrm{BZ}}, -\vec{q}, \mu)|^2 t^{2w+3\nu-2} \ , \qquad (4)$$

where a is a factor independent of wave vector $\vec{q}$ and polarization μ and insensitive to temperature, L is the "magnetostrictive" coupling coefficient, and $\vec{k}_{\mathrm{BZ}}$ is the point in the Brillouin zone where critical order-parameter fluctuations occur (Γ points for ordering due to direct interactions and M points for indirect). Furthermore, Matsushita has shown that $|L|^2$ is independent of $\vec{q}$ for longitudinal waves and is zero for all transverse waves except those associated with the shear elastic constant $C' = \frac{1}{2}(c_{11} - c_{12})$. However, Kawasaki's more general treatment[40] does not retain the temperature dependence indicated by the factor $t^{2w+3\nu-2}$, where w is a small but not well characterized critical exponent. Indeed, there are special difficulties in predicting the asymptotic temperature dependence of C for longitudinal waves in cubic Ising lattices.[46] The data to be presented below are consistent with the assumption that the value of the relaxation strength C for longitudinal waves in a given crystal at a given pressure is independent of temperature and direction of propagation. This assumption will be used in the analysis and will be discussed in Sec. III.

For the asymptotic behavior of the real and imaginary parts of $\hat{F}(\omega\tau)$, Kawasaki gives for a model with a nonconserved order parameter[40]

$$\begin{aligned} &\mathrm{Re}\hat{F} = \omega\tau \text{ and } \mathrm{Im}\hat{F} = -\omega^2\tau^2 \ \text{ for } \omega\tau << 1 \ , \\ &\mathrm{Re}\hat{F} \cong \text{const and } \mathrm{Im}\hat{F} \cong \text{const}' \ \text{ for } \omega\tau >> 1 \ . \end{aligned} \qquad (5)$$

Matsushita predicts a single-relaxation form for $\hat{F}$; that is,

$$\hat{F} = \hat{F}_1 \equiv \frac{\omega\tau}{1 + i\omega\tau} = \frac{\omega\tau - i\omega^2\tau^2}{1 + \omega^2\tau^2} \ . \qquad (6)$$

These two results are consistent at small $\omega\tau$, and there is experimental evidence to support the use of $\hat{F}_1$ up to $\omega\tau \simeq 1$. However, deviations from $\hat{F}_1$ are observed for large values of $\omega\tau$.

In summary, our analysis of longitudinal acoustic data along various isobars will be based on Eq. (2) with C taken to be independent of temperature. The value of τ at each temperature will be obtained from the ultrasonic attenuation data by taking $\hat{F}(\omega\tau)$ to be equal to $\hat{F}_1$ up to $\omega\tau = 1$; i.e.,

$$\frac{\alpha}{\omega} = C\frac{\omega\tau}{1 + \omega^2\tau^2} \ \text{ for } \omega\tau \leqslant 1 \ . \qquad (7)$$

All of the ultrasonic attenuation data are completely consistent with these assumptions. The resulting τ values are well correlated with neutron and NMR relaxation times far from T_c and show critical slowing down near T_c. Furthermore, the hypersonic values of α/ω and the dispersion D scale well at large values of $\omega\tau$ and conform with expectations based on Eqs.(5).

B. Longitudinal data in disordered phase

In four cases, there are sufficient ultrasonic attenuation data in the range $0.25 < \omega\tau < 1$ (10- and 30-MHz measurements at $t \lesssim 10^{-2}$) to allow one to determine the value of the strength C. The most extensive data for testing the validity of Eq. (7) with C taken as independent of temperature are those for NH_4Br.[2] One-atmosphere α values in the range $0.8 < \Delta T < 2.5$ K yield $C = 3.75$, in units of 10^{-8} sec cm^{-1}; while 3.25 kbar data in the $0.2 < \Delta T < 1.8$ K range lead to $C = 2.95$. For ND_4Cl at 1 atm, α values in the $0.5 < \Delta T < 2$ K range yield $C = 4.5$.[22] For NH_4Cl the C value is more difficult to establish (see Sec. III), but the best choice appears to be $C = 5.5$.

The relaxation times τ in the disordered phase resulting from the use of the above C values are shown in Figs. 2 and 3 and will be discussed in Sec. IV. Using these acoustic τ values, we have constructed plots of all available α/ω and D data for NH_4Br at 1 atm (Figs. 4 and 5) and NH_4Cl at 1 atm (Figs. 6 and 7). In each of these figures, the smooth curve indicates the variation predicted by Eq. (2) with $\hat{F} = \hat{F}_1$ and the specified C value. The single-relaxation form for $\hat{F}$ is in quite good agreement with both attenuation and dispersion up to $\omega\tau \approx 2$, but the data show that the form of $\hat{F}$ must change substantially for $\omega\tau > 2$. It is not possible to assess deviations of $\hat{F}$ from $\hat{F}_1$ in other cases since the necessary hypersonic data are not yet available. However, it should be noted that the single-relaxation curve pro-

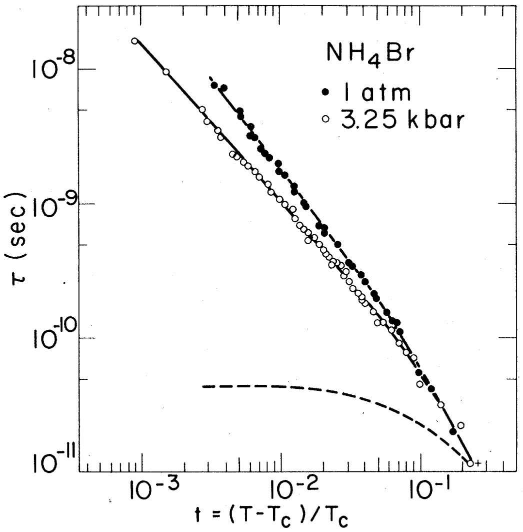

FIG. 2. Relaxation times in the disordered phase of NH_4Br at 1 atm and 3.25 kbar. Solid and open points represent values obtained from ultrasonic attenuation. The plus symbol denotes the value obtained from a Brillouin investigation at 1 atm and 297 K. The dashed curve represents the NMR correlation times at 1 atm.

vides an excellent fit to the ultrasonic attenuation up to $\omega\tau \simeq 1$ in NH_4Br at 3.25 kbar.

In addition to the measurements cited above, there are ultrasonic attenuation data for NH_4Br at 1.88 kbar,[2] and NH_4Cl at 1.5 kbar and other pressures in the range 0.5 to 3 kbar.[16,19] Unfortunately, these measurements only cover the range $\omega\tau \lesssim 0.2$, and it is not possible to determine a value for C. The values of the product $C\tau$ and their temperature variations are, however, known and are listed in Table II. In the case of NH_4Cl at 1.5 kbar, $(2.90\times10^{-19})\, t^{-1.1}$ is the expression quoted in Ref. 19 while $(1.73\times10^{-19})\, t^{-1.2}$ was obtained from our fit to these data. A precise characterization of the high-pressure NH_4Cl attenuation is not really possible since the data are sparse and moderately scattered.

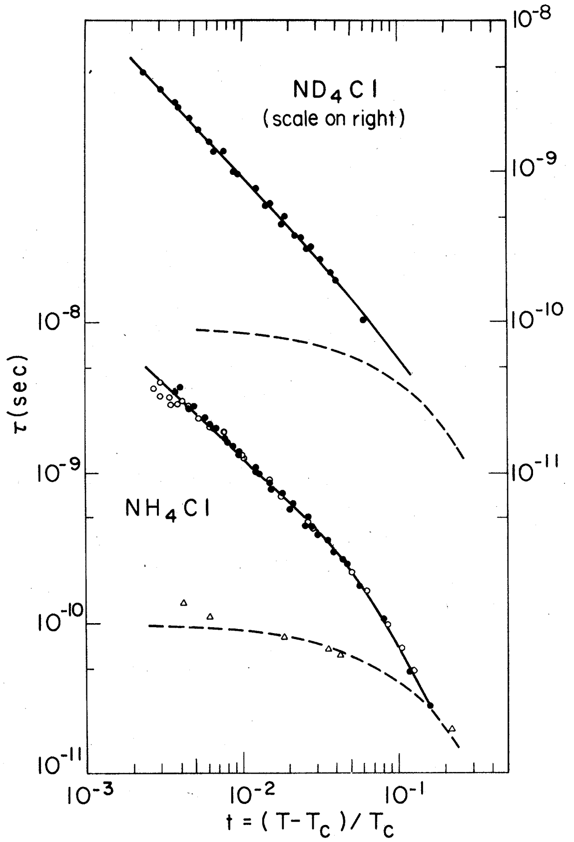

FIG. 3. Relaxation times in the disordered phase of NH_4Cl and ND_4Cl at 1 atm. NH_4Cl (scale on left)—Solid points are from 10 MHz-and 30 MHz-attenuation data determined in the present work; the open circles denote values obtained from the attenuation reported in Ref. 13; the triangles denote high-resolution neutron values of $1/\lambda_4$, where λ_4 is the rate on a single NH_4^+ ion going over the four-fold barrier between a given orientation and any of the six accessible opposite orientations. ND_4Cl (scale on right)—Solid points represent values obtained from attenuation data in Ref. 22. The dashed curves represent the NMR correlation times.

C. Transverse data in disordered phase

None of the ammonium halides show critical attenuation or dispersion of shear waves corresponding to the elastic constant c_{44}. However, C' shear waves do exhibit attenuation and dispersion in NH_4Br at 1 atm.[21–26] This effect diminishes with pressure: critical attenuation is quite weak near the triple point (1.66 kbar) and is absent at 1.88 kbar and above.[2] Thus the critical behavior of C' shear waves is clearly related to the tetragonal ordering that occurs in NH_4Br at low pressures. Unfortunately, the existing data do not extend to high enough values of $\omega\tau$ to permit an evaluation of τ along the lines given above. We note here only that the values of α_c/ω^2 for this transverse wave at 1 atm can be reasonably well represented by $(0.4\times10^{-19})\, t^{-1.43}\,\mathrm{sec}^2\,\mathrm{cm}^{-1}$ (see Ref. 21 for further details).

In view of the master phase diagram given in Fig. 1, one might expect that NH_4Cl at 1 atm would show some remnant of critical behavior for the C' shear wave. There is no evidence for this in the ultrasonic data,[12] and it can be shown[47] that the values of C' directly measured at 20 MHz are in good agreement with those calculated from hypersonic valocities at ~ 26 GHz over the range $1 < \Delta T < 50$ K.

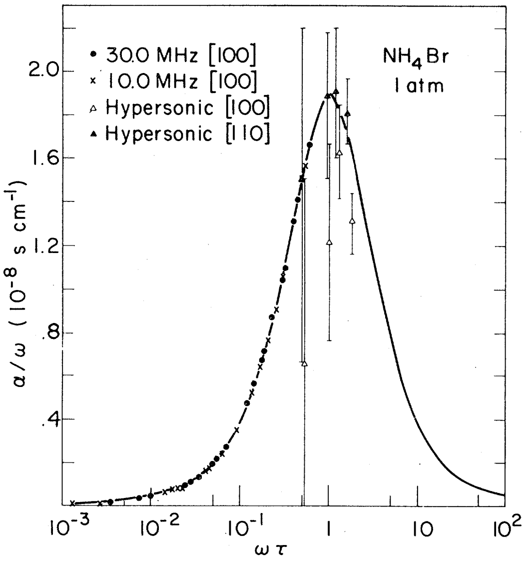

FIG. 4. Dependence of α/ω on $\omega\tau$ for NH_4Br at 1 atm. Ultrasonic data are from Ref. 2; hypersonic data with error bars are from Ref. 26. The solid line is the single-relaxation curve for $C=3.75\times10^{-8}$ sec cm^{-1}.

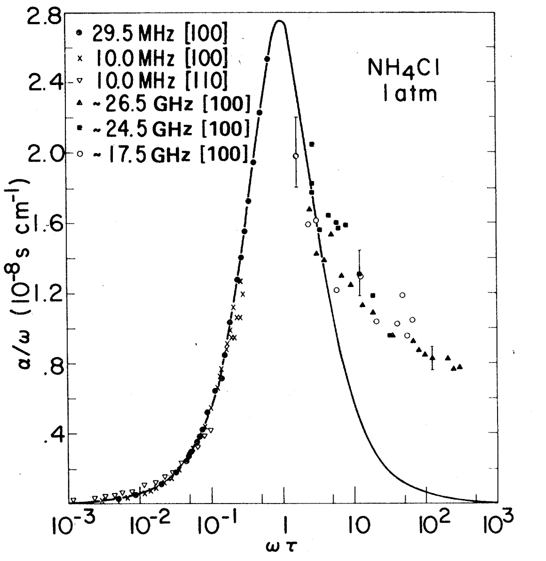

FIG. 6. Dependence of α/ω on $\omega\tau$ for NH_4Cl at 1 atm. Ultrasonic data are from Refs. 13 and 20 as well as from new measurements made in the present investigation; hypersonic data, with typical error bars, are from Ref. 25. The solid line is the single-relaxation curve for $C=5.5\times10^{-8}$ sec cm^{-1}.

D. Longitudinal data in ordered phases

Only a brief summary will be given of the acoustic results in the ordered phases since neither theory nor experiment are well developed. None of the available ultrasonic attenuation data below T_c show deviations from a quadratic frequency dependence; thus one cannot test Eq. (7) or determine relaxation times in the manner used in Sec. II B. Power-law representations of the quantity $\alpha_c/\omega^2\equiv(C\tau)_{\text{eff}}$ are given in Table II for comparison with the $C\tau$ values determined in the disordered phase.

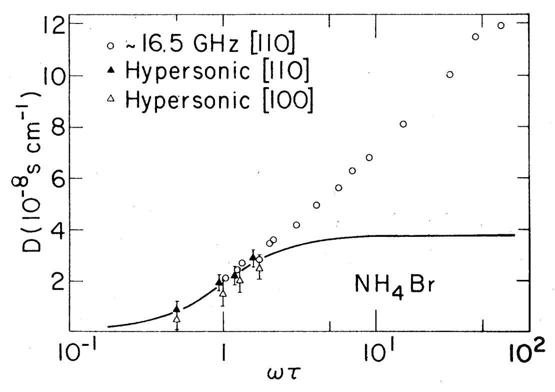

FIG. 5. Dependence of $D\equiv[u^2(\omega)-u^2(0)]/2u(\omega)u^2(0)$ on $\omega\tau$ for NH_4Br at 1 atm. The error bars are based on those given for $u(\omega)$ in Ref. 26. The solid line is a single-relaxation curve based on $C=3.75\times10^{-8}$ sec cm^{-1}.

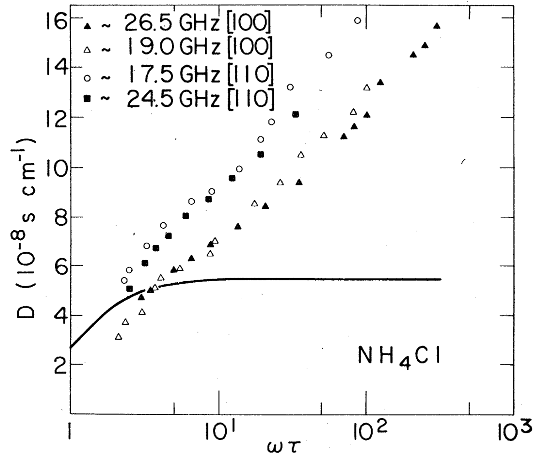

FIG. 7. Dependence of $D\equiv[u^2(\omega)-u^2(0)]/2u(\omega)u^2(0)$ on $\omega\tau$ for NH_4Cl at 1 atm. The solid line is a single-relaxation curve based on $C=5.5\times10^{-8}$ sec cm^{-1}.

TABLE II. Values of the relaxation strength C and the product $C\tau$, where τ is the critical acoustic relaxation time, in the disordered cubic phase of various ammonium halides. Also given are values of $(C\tau)_{\text{eff}} \equiv \alpha_c/\omega^2$ in the ordered phase, where a more detailed analysis is not presently possible.

Regime System, pressure	T_c (K)	Disordered Phase $C(10^{-8}$ sec cm$^{-1})$	 $C\tau(10^{-19}$ sec^2 cm$^{-1})$	Ordered Phase $(C\tau)_{\text{eff}}(10^{-19}$ sec^2 cm$^{-1})$
Tetragonal				
NH_4Br, 1 atm	234.5	3.75	$1.21\,t^{-1.38}$	$(130 \pm 30)t^{-0.75}$
Triple-point				
NH_4Br, 1.88 kbar	204.8	...	$13.6t^{-1.00}$	...
NH_4Cl, 1 atm	241.5[a]	5.5	$6.38t^{-1.0}$	...
Multicritical				
ND_4Cl, 1 atm	249.4	4.5	$2.64t^{-1.10}$	$10.0t^{-0.91}$
NH_4Cl, 1.5 kbar	256.0	...	$2.90t^{-1.1}$ or $1.73t^{-1.2}$	$8.9t^{-0.9}$
NH_4Br, 3.25 kbar	216.3	2.95	$1.22t^{-1.20}$	$13.0t^{-1.30}$

[a] Due to the first-order nature of this transition, the critical temperature associated with data in the disordered phase lies below the actual transition temperature (see Ref. 13).

In the case of ND_4Cl crystals,[22] values of α_c/ω^2 determined at 10 MHz over the range $-1.5 < \Delta T < -0.1$ K show deviations from a power-law fit that suggest that Eq. (7) with a constant C value can provide an adequate description of the cubic-ordered phase. Indeed, all the ordered-phase ND_4Cl data reported in Ref. 22 can be well represented ($\chi_\nu^2 = 1.3$) by Eq. (7) using $C = 5.0 \times 10^{-8}$ sec cm^{-1} and $\tau = (20 \times 10^{-12})\, t^{-0.91}$ sec. If this fitting procedure is valid, then the relaxation strength is almost the same in the disordered and cubic-ordered phases of ND_4Cl.

Comparable 10-MHz-attenuation data close to the transition also exist for NH_4Cl, but the metastability and hysteresis associated with the first-order character of this transition make it difficult to infer a relaxation strength from these data. However, the velocity dispersion between 20 MHz and ~ 19 GHz (see Refs. 19 and 23) makes it appear likely that the ordered-phase relaxation strength in NH_4Cl must be comparable to that in the disordered phase.

III. COMMENTS ON ACOUSTIC RELAXATION STRENGTH AND RELAXATION FUNCTION

A. Relaxation strength

We shall begin with a discussion of the temperature dependence of the relaxation strength C. Currently available data are not extensive enough to require that C be independent of temperature, but they do lend strong support to this assumption (see Figs. 4 and 6). The data for NH_4Br provide the best evidence. At 1 atm, the value $C = 3.75 \times 10^{-8}$ sec cm^{-1} obtained from ultrasonic data close to T_c ($\Delta T \simeq 1.5$ K) agrees quite well with two hypersonic values,[26] 3.3×10^{-8} and 4.0×10^{-8} sec cm^{-1}, obtained at room temperature ($\Delta T \simeq 60$ K). At 3.25 kbar, NH_4Br attenuation data are very well fit ($\chi_\nu^2 = 0.80$) using the constant value $C = 2.95 \times 10^{-8}$ sec cm^{-1} over the range $9 \times 10^{-4} < t < 3.6 \times 10^{-2}$. If C is assumed to follow the power-law variation $C_0 t^{-x}$, the fit is less good ($\chi_\nu^2 = 0.88$ for $x = \pm 0.1$, $\chi_\nu^2 = 1.11$ for $x = -0.2$, and $\chi_\nu^2 = 1.15$ for $x = +0.2$) due to systematic deviations in the small t range where $\omega^2\tau^2$ is not negligible compared to 1. Although the available ultrasonic data do not rule out a weak critical variation of the type $C_0 t^{-x}$ in other cases, the hypersonic data for NH_4Cl shown in Figs. 6 and 7 certainly scale well when a constant C is used.

Further support for the assumption of temperature independent C values is provided by the behavior of the acoustic relaxation times shown in Figs. 2 and 3. These τ values show critical slowing down close to T_c and join smoothly with the NMR relaxation times far from T_c. All of our C values were obtained from fitting data close to T_c. Any substantial monotonic variation in C with T would lead to physically unreasonable τ values at room temperature. The acoustic τ values should not lie below the NMR times, which characterize the microscopic time scale for uncorrelated reorientations of NH_4^+ tetrahedra.[48] On the other hand, the acoustic τ values should not be much larger than the NMR times at very large ΔT where no long-range cooperative effects persist. Indeed, in the case of NH_4Br at 1 atm there is direct evidence that acoustic and NMR times agree far from T_c. Figure 2 shows that the well established hypersonic value of τ at 297 K is in good agreement with the NMR correlation time and with the ultrasonic τ values based on a constant C.

In view of the above, large variations in C can definitely be ruled out but the possibility of a weak monotonic variation such as $C_0 t^{\pm 0.1}$ cannot be eliminated.[49] A better experimental determination of the behavior of C, including a test of the possibility that C might undergo nonmonotonic variations, will require data over a much wider frequency range. However, the new data presented in Refs. 2 and 22 are already sufficient to show that the method of evaluating C given in Refs. 19, 21, and 25 is not valid.

An improved theoretical prediction for the behavior of the relaxation strength in ammonium halides would also be welcome. In addition to a better definition of any possible temperature dependence, one would like to understand the pressure dependence of C. This is especially true in NH_4Br, where pressure changes the relative strengths of competing interactions and shifts the system from a tetragonal "antiferro" regime to a cubic "ferro" regime. In one aspect, Matsushita's theory[43] is already in satisfactory agreement with experiment. His prediction that C for a longitudinal wave should be independent of the direction of propagation is consistent with Figs. 4–6. The NH_4Cl dispersion data in Fig. 7 are less compatible with a $\vec{q}$-independent C, but the difference between $D_{[100]}$ and $D_{[110]}$ is due to the difference in $u^2(0)$ for these two directions and not due to any $\vec{q}$ dependence of $[u^2(\omega) - u^2(0)]$.[20] Another aspect of the Matsushita theory is the prediction of C' shear attenuation with the same temperature dependence as the longitudinal attenuation. In both these features, Matsushita's results differ from those obtained for structural transitions by Murata.[42]

B. Relaxation function

The real and imaginary parts of the complex relaxation function $\hat{F}(\omega\tau)$ can be directly inferred from Figs. 4, 6 and Figs. 5, 7, respectively. Unfortunately the most extensive high-frequency data are available for NH_4Cl, which is not as well behaved at 1 atm as either NH_4Br or ND_4Cl. However, the general behavior of $\hat{F}$ seems to be the same for all these systems: $\hat{F}$ corresponds to the single-relaxation form $\hat{F}_1$ up to $\omega\tau \approx 2$ and then shows a progressive change at larger $\omega\tau$ to the sort of form expected for a broad spectrum of relaxations. This "tail" at large $\omega\tau$ is very similar to the well known variation of $\hat{F}$ for a fluid near its critical point,[50] and the behavior of α_c/ω in Fig. 6 is compatible with Kawasaki's asymptotic prediction that Re$\hat{F}$ will become independent of $\omega\tau$ when $\omega\tau >> 1$. The principal qualitative difference between the form of $\hat{F}$ for ammonium halides and for critical fluids is the presence here of a strong low-frequency relaxation fairly well separated from the high-frequency spectrum. In order to clearly establish the nature of $\hat{F}$, new experimental work is needed, especially in the 100 MHz–10 GHz range.

IV. DISCUSSION

Our principal objective in this paper is to characterize the critical relaxation rate for ammonium halides in the disordered phase. The method of analysis has been shown to be consistent with the available data, and the acoustic τ values shown in Figs. 2 and 3 are qualitatively reasonable. Now we wish to test how well these relaxation times follow a simple power law of the form $\tau = \tau_0 t^{-\theta}$ and to compare the resulting "experimental" exponents θ with theoretical predictions for the critical exponent $z\nu$ given in Eq. (3).

The parameters τ_0 and θ obtained from a weighted least-squares fitting procedure are given in Table III. The variance for each τ value was obtained from the uncertainties in α_c, which ranged from 5% when $\Delta T > 5$ K to 8% when $\Delta T < 1$ K. In the case of NH_4Cl at 1.5 kbar and NH_4Br at 1.88 kbar, we cannot determine τ_0 but the values of the exponent θ resulting from a power-law fit to α_c/ω^2 are listed in Table III. As shown by the values of χ_ν^2, all the fits are good with the possible exception of NH_4Cl at 1 atm. In the latter case, there are complications due to the first-order instability, hysteresis, and presence of slip bands[51] in the disordered phase. As a result it is difficult to choose an unambiguous value for T_c and impossible to obtain data close to T_c. Furthermore, the fit was carried out with the merged data from two separate experiments. In any event, it can be seen from Fig. 3 that the somewhat scattered NH_4Cl data are certainly consistent with $\theta = 1$.

The critical exponents θ given in Table III exhibit different characteristic values for each of the three different regimes and lend additional support to the master phase diagram shown in Fig. 1. This diagram was based in part on various correspondences in the static elastic behavior, especially the close agreement between the variation of the longitudinal velocities $u(0)$ for NH_4Cl at 1 atm and NH_4Br at 1.88 kbar,[2] and for ND_4Cl at 1 atm and NH_4Cl at 1.5 kbar.[6] We now wish to compare the experimental θ values with presently available theoretical predictions for $z\nu$. In doing so, it should be kept in mind that the θ values may be subject to systematic errors of about ±0.1 due to the possibility that C should be represented in the form $C_0 t^{-x}$.

In order to obtain theoretical values for the exponent $z\nu$, one needs to specify a dynamical model and the possible conservation laws. Neither the complete Hamiltonian nor the equations of motion are

TABLE III. Least-squares values of the critical exponent θ and the coefficient τ_0 obtained from fitting τ values with the power law $\tau_0 t^{-\theta}$. The range of reduced temperatures $t \equiv (T-T_c)/T_c$ and the goodness of fit (χ_ν^2) are also shown.

Regime System, pressure	θ	$\tau_0\,(10^{-12}$ sec)	Range[a]	χ_ν^2
Tetragonal				
NH_4Br, 1 atm	1.38 ± 0.03	3.22	$4\times10^{-3} < t < 3.6\times10^{-2}$	1.16
Triple-point				
NH_4Br, 1.88 kbar	1.00 ± 0.03	...	$5.6\times10^{-3} < t < 6\times10^{-2}$	1.02
NH_4Cl, 1 atm	1.0 ± 0.05?	11.6	$1.9\times10^{-3} < t < 3.8\times10^{-2}$	3.3
Multicritical				
ND_4Cl, 1 atm	1.10 ± 0.03	5.86	$2\times10^{-3} < t < 3.7\times10^{-2}$	1.42
NH_4Cl, 1.5 kbar	~ 1.15	...	$3\times10^{-3} < t < 4\times10^{-2}$	...
NH_4Br, 3.25 kbar	1.20 ± 0.05	4.14	$0.9\times10^{-3} < t < 3.6\times10^{-2}$	0.80

[a] With the exception of NH_4Br at 1.88 kbar, the τ values systematically fall below the power-law curve when $t > 4\times10^{-2}$. The value of $t_{\min}$ is limited by high attenuation or complications due to scattering losses close to T_c (e.g., see Ref. 22).

yet well established for ammonium-halide crystals, but the pseudospin-phonon-coupled Hamiltonian used in Refs. 8 and 43 is the best available starting point. Unfortunately, none of the dynamic models yet studied by renormalization-group techniques involve a system with competing interactions. However, the general character of the ammonium halides suggests comparison with Hohenberg and Halperin's model A.[44] This time-dependent Ginsburg-Landau model for a single n-component order parameter is a purely relaxational model based on dissipative equations of motion with no conserved quantities. Another possibility to consider is model C, a relaxation model appropriate when the rate of thermal conduction is slow relative to the rate of order-parameter relaxation.[44] In this case, energy is essentially conserved. The important determining factor is the ratio $D_T\xi^{-2}/\Gamma_\xi$, where D_T is the thermal diffusivity $\lambda/\rho C_p$. If $D_T\xi^{-2}/\Gamma_\xi >> 1$, as is likely for ammonium halides, energy transfer will be rapid compared to order-parameter relaxation and model A will be appropriate. However, very close to T_c, the influence of C_p might cause this ratio to fall enough so that model C would become appropriate.

For model A, the dynamic exponent z for a second-order critical point is given by $z = 2 + c\eta$, where η is the small Fisher exponent and c is a weak function of spin dimensionality n and lattice dimensionality d.[44] Thus for $d = 3$, one finds $z \simeq 2.05$ for a second-order point. For model A near tricritical and higher-order critical points, the marginal dimensionality $d^* \leq 3$ and conventional van Hove theory is appropriate.[45] Thus, $z = 2$ in these cases. For model C, the exponent z is given by $z = 2 + \alpha/\nu$ for critical points of all orders when $n = 1$, but the situation becomes more complicated for $2 < n < 4$.[44,45] Thus for an Ising-like order parameter, one finds $z = 2.17$ for a second-order critical point, $z = 3$ for a tricritical point, and $z = 3.33$ for a fourth-order point. A summary of the theoretical values of the critical exponent $z\nu$ is given in Table IV for the available models most pertinent to our analysis.

1. *Tetragonal regime*

This regime, represented by NH_4Br at 1 atm, corresponds to a region of the phase diagram where fluctuations in the antiferro order parameter should be dominant. In this region ammonium halides are analogous to an anisotropic $n = 3$ antiferromagnet, since the tetragonal axis can be oriented along any of the original cubic axes. Although there is a first-order discontinuity and related hysteresis associated with the transition in NH_4Br at 1 atm, these features appear to be very weak[1,21] and it is likely that the properties near the transition are controlled by a critical fixed point. In this case, we should compare $\theta = 1.38$ with $z\nu$ for model A with $n = 3$. The exponents 1.37 and 1.43 given in Table IV for a cubic and isotropic Heisenberg fixed point are close to our experimental θ values, and they suggest that $z\nu$ is not very sensitive to details of the Hamiltonian once d and n are specified. A renormalization calculation for a more realistic Hamiltonian would be desirable, but the prospects are good that the tetragonal regime can be understood in terms of a $n = 3$ second-order fixed point and dynamical model A.

TABLE IV. Critical exponents $z\nu$ characterizing order-parameter relaxation for various theoretical models described in Refs. 44 and 45. The lattice dimensionality $d=3$ in all cases, and the order-parameter dimensionality n is specified. IFP, HFP, and CFP denote Ising, Heisenberg, and cubic fixed points, respectively.

Order of transition	Model A	Model C
Second order	1.28($n=1$, IFP)	1.39($n=1$, IFP)
	1.37($n=3$, CFP)	
	1.43($n=3$, HFP)	
Tricritical	1 (all n)	1.5 ($n=1$)
Fourth order	1 (all n)	1.67 ($n=1$)

2. *Triple-point regime*

This regime corresponds to a region where both the antiferro and the ferro order parameters should play an important role. The experimental exponent $\theta=1.0$ does not agree with any theoretical result for n-component models near a second-order transition but does agree with conventional theory ($z=2$ and $\nu=\frac{1}{2}$). This is somewhat puzzling in view of the topological analogy between the phase diagrams of ammonium halides and magnetic spin-flop systems.[52,53] If this analogy were valid and the order-disorder transitions were second order up to the triple point, the D-O_c-O_T triple point would be a "bicritical" point where $n=1$ and $n=3$ critical lines met. Critical behavior near such a bicritical point should be the same as that for a second-order transition in a model with a single $n=4$ order parameter, and one would expect $z\nu \gtrsim 1.4$ for model A. The failure of the experimental θ value to agree with this expectation may be due to the fact that there are small first-order instabilities along both the D-O_T and D-O_c transition lines near the triple point. This could imply that some kind of tricritical or high-order critical point lies nearby, in which case $z\nu=1$ for kinetic model A as indicated in Table IV. The first-order instabilities could also indicate a Landau-like transition in which fluctuations do not play an important role.

3. *Multicritical regime*

This regime in ammonium halides corresponds to a region of the phase diagram ~1.5 kbar above the triple point. In this region the ferro order parameter is dominant, but there are complications due to strong coupling between the order parameter and acoustic phonons and possibly NH_4^+ librational motions. The multicritical point marks the change from weakly discontinuous D-O_c transitions to continuous ones and presumably corresponds to a tricritical or higher-order critical point. However, the static critical behavior near this point is not yet understood,[2–4,22,54] and the interpretation of the dynamic results is difficult. In the context of model A, one would expect $z\nu=1$ at a multicritical point and $z\nu=1.28$ at a second-order Ising point. The experimental θ values in Table III lie between these two expectations.

There are several possible explanations for the multicritical results, none of which are conclusive. First, the use of a more-detailed Hamiltonian capable of explaining the static properties may yield a dynamic prediction for $z\nu$ different from those given in Table IV. Second, data obtained at p^* may exhibit crossover from tricritical to second-order exponents that is not obvious due to the limited experimental range in reduced temperature t. One argument against this possibility is the fact that θ for NH_4Cl does not show any meaningful trend as a function of pressure between 1.27 and 2.66 kbar.[19] Third, the experimental θ value could be reduced by 0.1 if one assumed that $C=C_0t^{-0.1}$. This would make ND_4Cl at 1 atm and perhaps NH_4Cl at 1.5 kbar agree with a model-A multicritical point, but the NH_4Br data at 3.25 kbar do not seem to allow[55] this sort of systematic "correction" (see Sec. III A.)

It should be noted that the temperature dependence of the elastic constant c_{11} indicates the static behavior of NH_4Br in the disordered phase at 3.25 kbar is somewhat different from that of the other two multicritical systems.[2] Furthermore, Table II shows that the dynamic behavior of NH_4Br in the *ordered phase* is at considerable variance with those of NH_4Cl and ND_4Cl. In the former case, α_c/ω^2 varies more rapidly with t and the ratio $\alpha_c(\text{ordered})/\alpha_c(\text{disordered})$ at any given t is about three times greater than that for the other systems. Such differences are in contrast to the very close similarity of both the static[22] and dynamic multicritical properties of ND_4Cl at 1 atm and NH_4Cl at 1.5 kbar.

V. SUMMARY

The dynamical aspects of critical phenomena in ammonium-halide crystals have been presented, and a wide variety of experimental data (some previously unpublished) have been analyzed in a coherent manner. It has been shown that all available acoustic data for a given system can be scaled with the choice of a single critical relaxation time. In all cases, the acoustic relaxation times *far from* the transition merge smoothly with the noncooperative NMR correlation times. The critical exponent characterizing the temperature dependence of the acoustic relaxation times *near* the transition has a different value for each of three regimes on the master phase diagram describing order-disorder phenomena in ammonium halides. These experimental results are compared with recent predictions for the rate of order-parameter relaxation in various theoretical models.

In the process of evaluating the critical relaxation times τ, several pieces of evidence are cited to show that the relaxation strength C is either independent of temperature or, at most, a very weakly varying function of the reduced temperature t. A definitive characterization of C will require new experiments over a wider range of frequencies. Such experiments could also establish the complex relaxation function $\hat{F}(\omega\tau)$ at large values of $\omega\tau$, the nature of which is only suggested by the sparse hypersonic data currently available.

Although experiments at higher frequencies would certainly refine and extend the analysis given here, we do not believe that they would substantially change the character of the dynamical behavior shown in Figs. 2 and 3. The most important aid to an improved characterization of critical relaxation in ammonium halides would be measurements at much smaller values of the reduced temperature. This can be achieved only in regimes free from first-order instabilities or hysteresis. It also requires very pure strain-free samples which hopefully will not develop strain inhomogeneities as an intrinsic result of ordering.

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