Important Generalization Concerning the Role of Competing Forces in Displacive Phase Transitions

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On the basis of an analysis of data on a large number of compounds exhibiting displacive phase transitions, it is observed (with no known exceptions) that the transition temperature *decreases* with hydrostatic pressure for those transitions associated with soft zone-center optic phonons and *increases* for those transitions associated with soft zone-boundary optic phonons. This difference in behavior is tentatively interpreted in terms of a reversal in the roles of the short-range and long-range forces in the lattice dynamics of the two cases.

In this Letter we report briefly the effect of hydrostatic pressure on the antiferrodistortive phase transition temperature in $BaMnF_4$ and thereby emphasize what appears to be an important generalization (with no known exceptions) about the nature of the delicate balance between competing forces responsible for soft-mode behavior in crystals exhibiting displacive structural phase transitions. High pressure strongly affects this balance of forces and appears to be the only variable which can support the conclusions to be drawn.

$BaMnF_4$ is an important member of a group of isomorphous crystals of the $BaM^{2+}F_4$ type (M = Mg, Zn, Mn, Fe, Co, and Ni). Recently a second-order (or nearly so) phase transition was discovered in this crystal at ~250°K ($=T_c$).[1,2] The transition is associated with the softening of an optical phonon at the zone boundary (z.b.) of the high-temperature orthorhombic ($C_{2v}{}^{12}$) phase and involves doubling of the primitive unit cell below T_c.[2] Thus this soft mode is qualitatively similar to the well-known z.b. soft modes in $SrTiO_3$ and $Gd_2(MoO_4)_3$. The similarity extends further in that the order parameter for the $BaMnF_4$ transition is also believed to be an angle of rotation of octahedra[2] (in this case MnF_6).

The effect of hydrostatic pressure on T_c of $BaMnF_4$ was determined from static dielectric constant measurements on oriented single-crystal samples. Details of the measurements and results will be published elsewhere. Here it suffices to indicate that small, but well-defined, anomalies in the dielectric constants are observed at T_c. For the crystal used, $T_c = 247.2$°K at 1 bar, and it increases with pressure with an initial slope $(dT_c/dP) = 3.3$°K/kbar. Table I compares this value with those obtained for a number of crystals exhibiting displacive phase transitions.

Table I reveals some important features which we now wish to dwell on. For some of the crystals in the table including $BaMnF_4$ the transitions are associated with soft z.b. optic phonons, whereas for others the transitions [ferroelectric (FE)] involve soft-zone center (z.c. or $\vec{q}=0$) TO phonons. In some cases (e.g., $SrTiO_3$, $PbZrO_3$, and $PbHfO_3$) the crystals possess both types of soft modes. Note that in all cases where the transition involves a z.c. TO mode T_c decreases with increasing pressure, whereas for those transitions involving z.b. optic modes T_c increases with increasing pressure.[3] This appears to be a general result for displacive phase transitions involving soft optic phonons to which we know of no exception. This result has important implications relating to the nature of the balance of forces which leads to the softening of the modes in the two cases.

The decrease of T_c with pressure for the displacive FE transitions can be readily understood from the well-known soft-mode theory.[4] In this

TABLE I. Temperature dependence of the transition temperature T_c for a variety of crystals which exhibit displacive structural phase transitions. Note that T_c increases with pressure for all transitions associated with zone boundary (z.b.) soft optic phonons whereas the opposite is true for all transitions associated with zone center (z.c.) optic phonons.

Crystal	Mode (Sym.)	T_c[a] (°K)	dT_c/dP (°K/kbar)	Ref.
$BaMnF_4$	z.b.	247.3	3.3	This work
$Gd_2(MoO_4)_3$	z.b.	435	29.5	Shirokov et al.[c]
$SrTiO_3$	z.b. (R_{25})	110	1.7	Sorge et al.[d]
"	z.c. (Γ_{15})	36	-14.0	Samara[e]
$KMnF_3$	z.b. (R_{25})	186	3.0	Okai & Yoshimoto[f]
$CsPbCl_3$	z.b. (M_3)	320	7.6	Gesi et al.[g]
"	z.b. $(R_{25})^b$	315	5.2	"
"	z.b. $(R_{25})^b$	311	5.4	"
$PbZrO_3$	z.b.	507	4.5	Samara[h]
"	z.c. (Γ_{15})	475	-16.0	"
$PbHfO_3$	z.b.	434	5.9	"
"	z.c. (Γ_{15})	378	-10.0	"
$BaTiO_3$	z.c. (Γ_{15})	393	-5.2	Samara[e]
$PbTiO_3$	z.c. (Γ_{15})	765	-8.4	"
SbSI	z.c.	292	-37.0	Samara[i]
$Pb_5Ge_3O_{11}$	z.c.	450	-6.7	Gesi & Ozawa[j]

[a] T_c is either the actual transition temperature or the Curie-Weiss temperature deduced from the static susceptibility.

[b] These modes derive from the R_{25} mode of the cubic phase.

[c] A. M. Shirokov *et al.*, Fiz. Tverd. Tela 13, 3108 (1972) [Sov. Phys. Solid State 13, 2610 (1972)].

[d] G. Sorge *et al.*, Phys. Status Solidi 37, K17 (1970).

[e] G. A. Samara, Ferroelectrics 2, 277 (1971).

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[g] K. Gesi *et al.*, J. Phys. Soc. Jpn. 38, 463 (1975).

[h] G. A. Samara, Phys. Rev. B 1, 3777 (1970).

[i] G. A. Samara, Phys. Lett. 27A, 232 (1968).

[j] K. Gesi and K. Ozawa, Jpn. J. Appl. Phys. 13, 897 (1974).

case the vanishing (or near vanishing for a first-order transition) of the soft-mode frequency ω_s at T_c results from the cancelation of the short-range forces by the Coulomb forces. Formally ω_s is given (in the harmonic approximation) by

$$\mu\omega_s^2 = R - [(Ze^*)^2/v]C(0), \tag{1a}$$

where μ is the appropriate reduced mass, (Ze^*) is the effective ionic charge, v is the unit cell volume, $C(0)$ is the electrostatic force constant for the $\vec{q}=0$ mode, and R is the sum of the appropriate short-range force constants. Thus it is seen that ω_s is given by the difference between a short-range (SR) interaction and a long-range (LR) interaction, i.e.,

$$\omega_s^2 \propto [\text{SR interaction}] - [\text{LR interaction}]. \tag{1b}$$

Actually, in the harmonic approximation there is an overcancelation of the SR interaction by the LR term leading to an imaginary soft-mode frequency. It is the anharmonic interactions which then stabilize ω_s and make it real at zero pressure. However, for the purposes of the qualitative arguments to follow, it suffices to consider the harmonic result, Eqs. (1).[5] Specifically, we note that decreasing the interionic distance r by pressure increases the SR interactions ($\sim r^{-n}$, where n is a large number $\simeq 10$) much more rapidly than the LR interactions ($\sim r^{-3}$) leading to an increase in ω_s and thereby a decrease in T_c. This can be most readily seen from the usually observed temperature dependence of ω_s, namely

$$\omega_s^2 = K(T - T_c), \tag{2}$$

where K is a positive constant. A larger ω_s at constant T necessitates a lower T_c. Alternatively, as the strictly harmonic value of the soft-mode frequency becomes less negative with increasing pressure we do not need to go to as high a temperature ($\equiv T_c$) to stabilize ω_s and make it real. Ultimately at sufficiently high pressure we expect the strictly harmonic frequency of this mode to become real and under such a circumstance the crystal will be stable with respect to this mode at all temperatures, i.e., $T_c \to 0$°K. This vanishing of T_c has been observed experimentally.[6]

For the transitions associated with the z.b. phonons the situation is evidently different. Here the increase of T_c with pressure can be interpreted as resulting from the softening of the soft-mode frequency with pressure. Phenomenologically this can be readily seen from Eq. (2) which also holds for z.b. soft phonons; however, we seek a more physical argument. The clue is suggested by the results of lattice-dynamical calculations. Such calculations are apparently available in sufficient detail only for $SrTiO_3$, but we believe that the results are qualitatively true for other soft-z.b. optic phonons. For $SrTiO_3$, and the cubic ABO_3 perovskite structure in general, the characteristic frequencies of the T_2 phonon branch along the $[\frac{1}{2}\frac{1}{2}\xi]$ direction, which is compatible with the modes M_3 and R_{25} (see Table I) at $\xi = 0$ and $\frac{1}{2}$, respectively, can be written as

$$\mu\omega^2(T_2) = R' + [(Ze^*)^2/v]C(\xi), \tag{3}$$

where R' is the sum of the appropriate short-range force constants and $C(\xi)$, which is different from $C(0)$ in Eq. (1a), represents the electrostatic interactions. Analysis of available calculations based on rigid-ion and shell models[7,8] shows that the sum R' is strongly negative. This result and its implications do not appear to have been emphasized earlier. It thus appears that for the Γ_{25} and M_3 soft modes, the balance of forces leading to an imaginary harmonic mode frequency is due to the overcancelation by the short-range interactions which are negative, i.e., attractive. In the case of the zone center FE mode, on the other hand, the overcancelation is by the negative Coulomb forces. In other words, for the M_3 and R_{25} z.b. modes in $SrTiO_3$ the roles of the short-range and electrostatic forces are reversed from those for the $\vec{q}=0$ FE mode. This reversal is also clearly seen from the recent results of Yoshimitsu[9] who analyzed the dispersion curves of $SrTiO_3$ along the [111] direction over the whole Brillouin zone on the basis of a rigid-ion model. Specifically, Yoshimitsu found that the R_{25} mode is stabilized by the LR interactions and destabilized by the SR interactions which are negative. The opposite is true for the $\vec{q}=0$ FE mode (Γ_{15}).

We suggest that the above-discussed reversal of the roles of SR and LR forces from what they are for z.c. optic phonons obtains not only in $SrTiO_3$, but rather, it may be the general rule for displacive transitions involving soft z.b. optic phonons. The pressure results in Table I provide support for this hypothesis. In fact, pressure is a unique and all-important variable in this regard. By pressure we simply reduce the interionic separation and thereby change the balance between the competing forces. By analogy to Eq. (1b), it is then tempting to express the soft z.b. phonon frequency schematically as

$$\omega_s^2 \propto (\text{LR interaction}) - (\text{SR interaction}). \quad (4)$$

In this case the LR interaction can generally be expected to be small and to exhibit a weaker r dependence than will the SR interaction. The explanation for the increase in T_c with pressure then follows from arguments similar to those advanced earlier in the paper. The strictly harmonic frequency of the mode gets more negative with increasing pressure, and we need to go to higher T to provide the anharmonic contributions necessary to stabilize ω_s, i.e., a higher T_c.

In conclusion, we consider the essence of this paper to be the apparent generalization of behavior that we bring to light. We believe that this finding is important and may hold a key to the better understanding of the nature of the transitions in questions. At present we know of no exceptions to the rules noted; however, the possibility of such exceptions cannot be completely ruled out. The explanations given are qualitative and, in the z.b. case, tentative. Providing a more detailed and deeper explanation of the results is the main challenge that the paper poses.

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[3] The list of z.b. transitions in Table I includes both antiferroelectric, i.e., antipolar transitions (e.g., $PbZrO_3$ and $PbHfO_3$) as well as transitions which do not involve polar modes (e.g., M_3 and R_{25}). Although it is recognized that there are differences between the two cases, nevertheless both involve z.b. optic phonons and both behave qualitatively the same under pressure, thus suggesting that the dominant interaction may be similar in the two cases. This is an assumption.

[4] W. Cochran, Adv. Phys. 9, 387 (1960).

[5] It should be emphasized that the interesting and unusual properties of ω_s are not so much a consequence of large anharmonicities as they are a result of the extremely small harmonic frequency of the mode caused by the almost perfect cancelation of SR by LR interactions as in Eqs. (1). This point was emphasized by R. A. Cowley, Phys. Rev. 134, A981 (1964).

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