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Raman scattering study of the ferroelastic transition of LaP_5O_{14} under hydrostatic pressure

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The effect of a hydrostatic pressure ($p \leq 2$ kbar) on the second-order ferroelastic transition of LaP_5O_{14} has been investigated using a gaseous high-pressure cell in a polarized Raman scattering experiment. The critical temperature T_c increases linearly with pressure ($dT_c/dp = +21.1 \pm 0.5$ K/kbar) in agreement with the Landau free energy previously determined for this material. The maximum linewidth of the B_{2g} soft optic mode increases with pressure. On the other hand, its minimum frequency remains unchanged. This behavior rules out the role of the coupling of the soft optic mode to the strain as a possible cause of the anomalous positive sign of dT_c/dp. The influence of harmonic and anharmonic interactions on dT_c/dp is discussed.

I. INTRODUCTION

Isostructural rare-earth pentaphosphates (RP_5O_{14} with R = La to Tb) undergo a second-order ferroelastic transition with the symmetry change $mmm \rightarrow 2/m$ in the range 125 °C (for LaP_5O_{14}) to 174 °C (for TbP_5O_{14}).[1-3] Raman[4-7] and Brillouin[8,9] scattering experiments have shown that the main feature of the transition is the existence of a strong linear coupling between an underdamped soft optic mode of B_{2g} symmetry (A_g in the ferroelastic phase) and the spontaneous monoclinic shear e_5.[10-12] As a result, the softening of this optic mode in the prototype phase induces the vanishing of the elastic constant c_{55} related to e_5 (Refs. 8 and 9) at the ferroelastic transition. Besides, another softening optic mode of B_{3g} symmetry (B_g in the ferroelastic phase) has also been reported.[5,6]

The temperature dependences of the frequencies of the soft acoustic and optic modes and of the monoclinic spontaneous shear have shown that these quantities possess a strictly classical behavior[12] in the vicinity of the transition temperature. A quantitative phenomenological mean-field theory has been developed which accounts well for most of the available data.[12] This theory predicts that T_c should increase with hydrostatic pressure according to $dT_c/dp = (18.9 \pm 2.0)$ K/kbar. Partial Raman experiments briefly reported by Peercy on TbP_5O_{14} (Ref. 13) and $La_{0.5}Nd_{0.5}P_5O_{14}$ (Ref. 14) appear in good agreement with this value. However, Asaumi *et al.* have recently reported a much larger value of 38 K/kbar deduced from birefringence measurements on NdP_5O_{14}.[15] Therefore, there is a large experimental uncertainty on the value of dT_c/dp, but the sign of this quantity seems well established. As pointed out by Samara,[16] this sign is exceptional and anomalous for a transition driven by a zone-center optic mode. In this paper, we report a thorough Raman scattering study under hydrostatic pressure of the transition in LaP_5O_{14} in order to specify the value of dT_c/dp and clarify the anomalous pressure dependence in this family of materials.

II. EXPERIMENTAL PROCEDURE

The hydrostatic pressure was supplied by a Nowa-Swiss compressor and a pressure multiplier (0–7 kbar) with argon as the pressure-transmitting medium. Pressure was measured on a Heise spiral-type precision manometer placed near the multiplier on the 10-m-length pipe linking the multiplier to the pressure cell. Its calibration was checked by means of an electronic manometer using the pressure-dependent resistance of a manganine resistor. The pressure was read out with an accuracy of ± 10 bars and kept constant during the time necessary to record a spectrum.

The commercially purchased pressure cell (useful volume: 2 cm^3) was made of special steel and provided with three windows to allow optical measurements. These windows, made of corundum possessing some birefringence, were oriented with care to avoid a mixing of the spectra related to different polarizations of the exciting and scattered light. The additional birefringence induced in the windows by the pressure was found to be negligible.

The pressure cell was placed inside a temperature-regulated furnace. The temperature of the sample was measured by a Chromel-Alumel thermocouple, the head of which was located in a rigid metallic envelope inside the useful volume of the pressure cell at approximately 18 mm of the sample. The temperature gradient in the cavity was measured to be smaller than 0.15 K/mm.

The sample was a polished parallepipedic crystal of size $3 \times 3 \times 5$ mm^3 grown in our laboratory according to a previously described procedure.[17] Its faces were cut perpendicularly to the principal axes of the orthorhombic faces in order to study the soft B_{2g} and B_{3g} optic modes in the respective $x(zx)z$ and $x(zy)z$ scattering geometries. No particular care was needed because of the existence of ferroelastic domains since the directions of the crystallographical axes of the monoclinic phase vary only slightly from one domain to another.[2,3]

An unwanted heating of the sample by the laser beam could be detected from examination of the Raman spectra when we used the 600-mW 5145-Å line of an argon laser. It was found to be due to an absorption of the light by traces of grease carried by the argon gas used as the pressure-transmitting medium. The laser power was subsequently reduced to 150 mW and the heating effect then became negligible.

The scattered light was collected at right angle with a 125-mrad acceptance and analyzed using a triple Coderg monochromator. The instrumental linewidth was 2.4 cm^{-1} and the central frequencies of the Raman lines could be determined with an accuracy of ± 0.2 cm^{-1} for the B_{2g} and ± 0.3 cm^{-1} for the B_{3g} mode, the intensity of which was weaker.

III. RESULTS

Typical $x(zx)z$ Raman spectra obtained for various pressures at 140 °C are shown on Fig. 1.

On Fig. 2, we have plotted the pressure and temperature dependences of the frequencies of the Raman lines related to the two soft modes. For a given pressure, these frequencies increase on both sides of the transition temperature $T_c(p)$ which appears as a sharply defined minimum in the variation of ω. The plots are shifted towards higher temperatures as the pressure is increased, showing that T_c increases with pressure. At $p = 1$ bar, we find $T_c = 121.7 \pm 0.5$ °C while previous experiments[5,8,12] had indicated slightly higher values of T_c ($T_c \simeq 124$ or 125 °C). This difference is consistent with the measured gradient of temperature inside the cell between the sample and the thermocouple. Comparisons with previous measurements of the frequency of the B_{2g} mode[5] show that this gradient is nearly constant between 100 and 200 °C. In the considered range of pressures, T_c remains in this temperature interval and therefore the gradient does not prevent an accurate determination of the pressure dependence of T_c. On Fig. 3, we can see that T_c depends linearly on the pressure with a slope $dT_c/dp = +(21.1 \pm 0.5)$ K/kbar.

The two measured soft modes remain underdamped in the entire range of temperatures and pres-

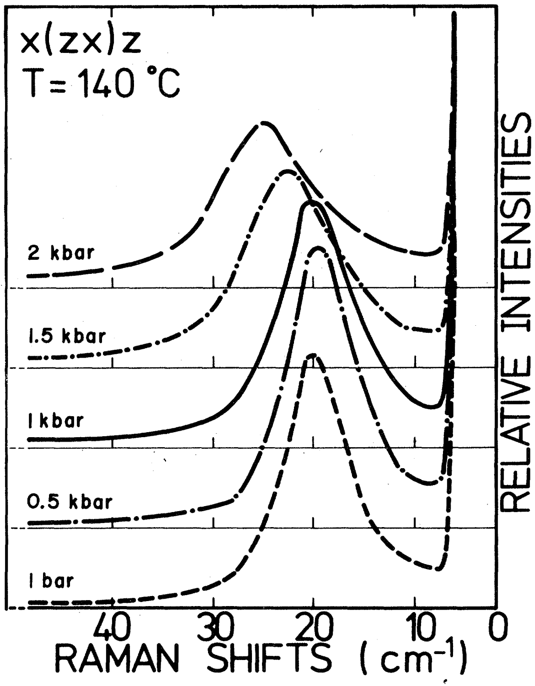

FIG. 1. Pressure dependence of the low-frequency $x(zx)z$ Raman spectra at 140 °C. For this temperature, the pressure transition is near 860 bars.

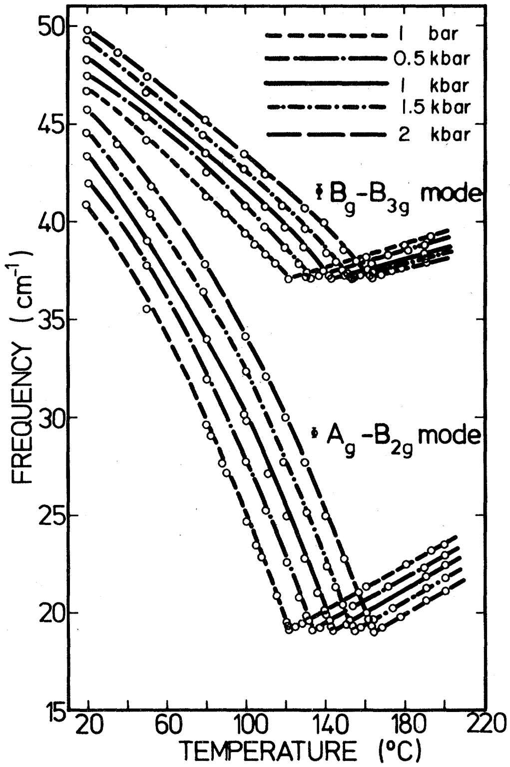

FIG. 2. Temperature and pressure dependences of the frequencies of the two soft optic modes of LaP_5O_{14}. The main effect of the hydrostatic pressure is a shift of the $p = 1$ bar curve towards higher temperatures.

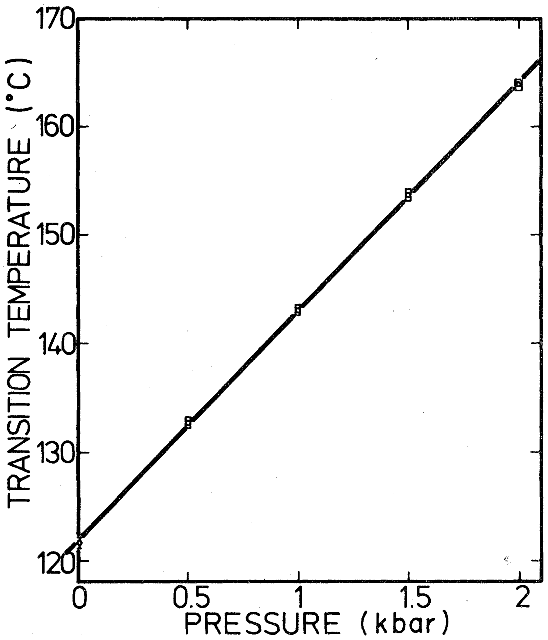

FIG. 3. Pressure dependence of the ferroelastic transition temperature leading to $dT_c/dp = 21.1 \pm 0.5$ °C.

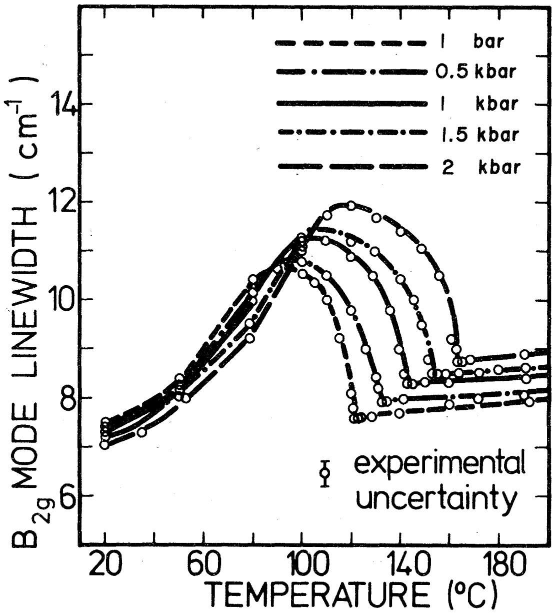

FIG. 4. Temperature and pressure dependences of the B_{2g} soft-mode linewidth (uncorrected from instrumental linewidth: 2.4 cm^{-1}).

sures. The linewidth of the upper B_{3g} mode is approximately 7 cm^{-1}. We have not been able to determine its variations because we could not avoid an overlap of this line with the much stronger B_{2g} line. Fortunately this overlap does not perturb significantly the determination of the linewidth of the B_{2g} line. This quantity is plotted on Fig. 4. As has been reported previously[5] from measurements at room pressure, the linewidth reaches a maximum some 35–40 °C below T_c. The same behavior is noted at higher pressures. To our knowledge, such a behavior is unique in materials undergoing a displacive phase transition, since in all cases investigated up to now the linewidth of the soft mode is maximum at the transition temperature. On the other hand, we observe that at a given temperature interval $[T - T_c(p)]$ below the transition, the linewidth increases with pressure. Its maximum varies from (10.6 ± 0.25) to (12 ± 0.25) cm^{-1} between 1 bar and 2 kbar. In principle, such a broadening could also arise from a stray effect, induced by a 15% inhomogeneity of the pressure inside the sample. However, since the sample is surrounded by argon fluid and is not clamped by any rigid sample holder, the pressure is likely to be perfectly hydrostatic and homogeneous. This is supported by the observation that the transition consists of a sharp minimum with no rounding of the $\omega(T)$ curve (see Fig. 2). Thus it is clear that the soft mode becomes more damped with increasing pressure. An extrapolation of our data shows that critical damping would be reached at about 20 kbar.

TABLE I. Minimum frequencies and temperature dependences of the squared frequencies of the two soft modes for various pressures. The damping correction has been taken into account.

		B_{2g} mode			B_{3g} mode		
Pressure (kbar)	Transition temperature (°C)	Minimum frequency ω_0 (cm^{-1})	$\left(\frac{\partial\omega^2}{\partial T}\right)_p$ Above T_c (cm^{-2}K^{-1})	Below T_c	Minimum frequency (cm^{-1})	$\left(\frac{\partial\omega^2}{\partial T}\right)_p$ Above T_c (cm^{-2}K^{-1})	Below T_c
0	121.6±0.5	19.7 ±0.2	2.46±0.12	12.34±0.4	37.0±0.3	2.35±0.35	7.64±0.5
1	143.1±0.5	19.75±0.2	2.41±0.16	11.98±0.4	37.0±0.3	2.25±0.50	7.61±0.5
2	163.8±0.5	19.8 ±0.2	2.44±0.22	11.95±0.4	37.1±0.3	2.20±0.60	7.54±0.5

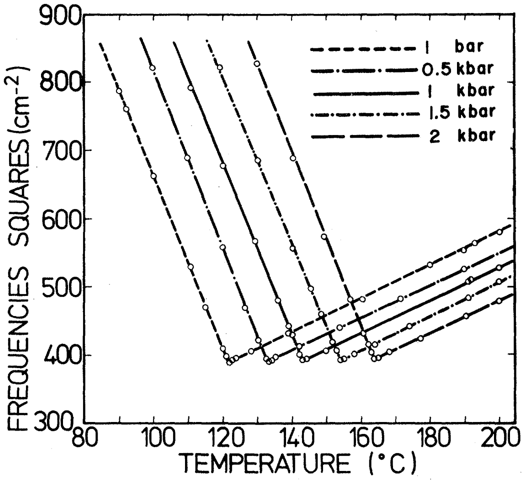

FIG. 5. Temperature and pressure dependences of the frequency squared of the B_{2g} mode. (The damping correction has been taken into account). It linearly varies on both sides of $T_c(p)$ in agreement with the classical mean-field behavior of LaP_5O_{14}.

Aside from the transition shift, pressure does not seem to affect the shape of the variations of the soft-mode frequencies. Their minimum values at the transition point appear to keep a constant value. Likewise their slopes on either sides of the transition seem unchanged. However, we can note that the experimental frequencies should be corrected since the damping of the modes is not negligible compared to their frequency. Using a usual damped harmonic oscillator model and taking into account the instrumental linewidth, one finds that this correction varies between +0.25 and +0.8 cm^{-1} for the B_{2g} mode, and between +0.2 and +0.3 cm^{-1} for the B_{3g} mode. The corrected minimum frequencies of the two modes are given in Table I for various pressures.

The corrected squared frequencies of the two soft modes depend linearly on the temperature on both sides of the transition as shown on Fig. 5 for the B_{2g} mode. The corrected slopes are also indicated in Table I.

IV. DISCUSSION

The results can be compared with previous high-pressure experimental data. From the Raman measurements performed by Peercy on TbP_5O_{14} (Ref. 13) and $La_{0.5}Nd_{0.5}P_5O_{14}$,[14] we can deduce $dT_c/dp = +18$ K/kbar which is close to the value determined in this work: 21.1 ±0.5 K/kbar. By contrast, Asaumi *et al.*[15] have inferred from birefringence measurements a higher value for the initial slope of T_c: $dT_c/dp = 38 \pm 2$ K/kbar. However their work shows measurements at only two pressures up to 9 kbar with experimental points not aligned with the room-pressure value. Careful inspection of their data discloses that the average slope in this pressure range is rather 25 K/kbar, in better agreement with our measurements. We can also note that their experiment has been performed with a diamond anvil cell on very small samples with the pressure measured using the pressure dependence of the fluorescence spectrum of ruby. This technique, which has the advantage of allowing one to reach very high pressures, is likely to yield less accurate values in the kbar range than the standard technique used in this work and applied to much larger samples.

For a second-order transition, the shift of the transition temperature can be related to other quantities through the thermodynamic Ehrenfest relation[18]:

$$\frac{dT_c}{dp} = T_c \frac{\Delta\left[\frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_p\right]}{\Delta\left[\frac{1}{v}C_p\right]} , \qquad (1)$$

where $\Delta[(1/v)(\partial v/\partial T)_p]$ and $\Delta[(1/v)C_p]$, respectively, represent the jumps, at the transition, of the volume thermal-expansion coefficient and of the specific heat per unit volume at constant pressure.

This formula can be tested making use of the experimental values of ΔC_p determined by Loiacono[19] for the neodymium isomorph and of the thermal-expansion coefficients previously obtained by standard dilatometry.[12] It supplies $dT_c/dp = (16.7 \pm 4)$ K/bar for NdP_5O_{14}, which is slightly smaller than the value obtained here for LaP_5O_{14}. The quantities involved in Ehrenfest's relation can also be derived from the Landau free energy of the transition,[12] provided its coefficients are numerically known. Actually, these have recently been fitted to the temperature dependences of the Brillouin spectra and the spontaneous shear of LaP_5O_{14}.[12] On this basis, we were able to derive a theoretical value of $dT_c/dp = (18.9 \pm 2)$ K/bar in good agreement with the present experimental data.

The preceding Landau theory does not only allow a correct prediction of the value of dT_c/dp. It also provides an interpretation of other features of the pressure dependence of the Raman spectrum. In the theory developed in Ref. 12, it was shown that the B_{2g} soft optic mode is the primary instability which monitors the transition and that its squared frequency increases linearly on both side of T_c. Above T_c, we have

$$\omega^2 = \omega_0^2 + a(T - T_c) \ . \qquad (2)$$

Because of the linear coupling between the soft optic mode and the spontaneous monoclinic shear e_5, the ferroelastic transition does not occur when ω vanish, but when the elastic constant c_{55} related to e_5 vanish. Thus, at T_c, the soft optic mode frequency takes a minimum value ω_0 related to the coupling coefficient γ by

$$\omega_0^2 = \frac{\gamma^2}{c_{55}^0} = a(T_c - T_0) \quad . \tag{3}$$

T_0 and c_{55}^0 would be, respectively, the transition temperature and the elastic constant in the absence of the coupling.

A straightforward calculation shows that formula (2) is again valid at high pressures if we replace T_c by $T_c(p)$ with $T_c(p)$ deduced from the Ehrenfest formula (1).

Thus, one expects that the linear temperature dependence of ω^2 will be kept under a hydrostatic pressure in conformity with the experimental results. The additional information one obtains from the measurements is that the three coefficients γ^2/c_{55}^0, a, and a' are not pressure dependent or are very slightly so, since as shown in Table I, no significant change is detected in the minimum values of the soft mode frequencies or in their slopes.

Let us now discuss the positive sign of dT_c/dp. Samara has noticed and justified that dT_c/dp should be negative for all displacive ferroelectrics whose transition is induced by a Brillouin-zone-center soft optic mode. This rule is clearly also obeyed by ferroelastic materials such as $\mathrm{BiVO_4}$ ($dT_c/dp = -16.6$ K/kbar[20]) and $\mathrm{KH_3(SeO_3)_2}$ ($dT_c/dp = -5.0$ °C/kbar[21]). These materials are very similar to $\mathrm{LaP_5O_{14}}$ since their transition is also believed to be induced by a strong linear coupling between a zone-center soft optic mode and an acoustic one. Even qualitatively the strength of the coupling is comparable in the three materials, since, as shown by formula (3), this strength can be measured by the difference $(T_c - T_0)$ which is 163 K for $\mathrm{BiVO_4}$,[20] 137 K for $\mathrm{KH_3(SeO_3)_2}$,[22] and 161 K for $\mathrm{LaP_5O_{14}}$.[5,12] Thus, as already noticed by Samara[16] and Peercy,[13] rare-earth pentaphosphates constitute an exception to Samara's rule. KCN ($dT_c/dp = +2$ K/bar)[23] and $\mathrm{TeO_2}$ ($dT_c/dp = +207$ K/kbar),[24] which are also "zone-center" ferroelastics, do not however possess an optic soft mode but only a soft acoustic one.

To discuss this result, let us, following Cowley[25] and Samara,[16] decompose the squared frequency of the B_{2g} soft mode into two contributions: a temperature-independent harmonic one (ω_h^2) and an anharmonic one (ω_anh^2) proportional to the absolute temperature over a large range of temperatures. Identification with (2) gives

$$\omega_\mathrm{h}^2 = -aT_0, \quad \omega_\mathrm{anh}^2 = aT \tag{4}$$

and

$$\omega^2 = \omega_\mathrm{h}^2 + aT, \quad \text{for } T > T_c \quad . \tag{5}$$

At $T = 0$ K, the extrapolated squared frequency of the B_{2g} mode is equal to ω_h^2 which is negative since the prototype phase is unstable in this temperature range. In the mechanically clamped crystal implicitly considered by Samara, this phase is stabilized above T_0:

$$T_0 = -\omega_\mathrm{h}^2/a \tag{6}$$

by the anharmonic contribution. In order to account for the pressure dependence of T_0, Samara assumes that dT_0/dp is dominated by the harmonic contribution. On the other hand, this harmonic contribution itself is the result of two types of interactions: positive short-range ones increasing rapidly with pressure, and negative long-range ones, whose increase with pressure is slower. Thus, by applying the pressure, ω_h^2 will become less negative and T_0 will be displaced towards lower temperatures. In order to restore the consistency of the behavior of rare-earth pentaphosphates with the preceding argument we can examine the conjecture of Peercy[14] and Samara[26] that in this case, the onset of ferroelasticity would play an essential role. In this view let us consider the transition temperature in the unclamped crystal. In this state, the coupling to the strain leads to the stabilization of the prototype phase at a temperature T_c higher than T_0. Formulas (3) and (6) give

$$T_c = (-\omega_\mathrm{h}^2 + \omega_0^2)/a \quad . \tag{7}$$

For this temperature the soft mode frequency reaches its minimum value ω_0. A positive sign for dT_c/dp could be determined by an increase of ω_0^2 with pressure. The experimental results (Table I) actually show that the variations of ω_0, if any, are smaller than 0.2 $\mathrm{cm^{-1}}$/kbar, which, all other quantities equal, would determine

$$\left|\frac{dT_c}{dp}\right| < 3.4 \text{ K/kbar} \quad , \tag{8}$$

an order of magnitude smaller than the experimental value. It therefore appears that the coupling between the soft optic mode and the strain cannot play the main role in explaining the anomalous pressure dependence of $\mathrm{LaP_5O_{14}}$. As shown by Eq. (7) we are therefore left, to account for the dependence of T_c, with the pressure dependences of ω_h^2 or of a.

Following Samara,[16] the harmonic term can be written

$$\omega_\mathrm{h}^2 = A\left(\frac{r_0}{r}\right)^n - B\left(\frac{r_0}{r}\right)^m \quad , \tag{9}$$

where r_0 and r are the characteristic unit-cell dimension, respectively, at $p = 0$ and $p > 0$. The first term is the short-range contribution with $n \approx 10$. The second term represents the long-range interactions. Unlike the case of ferroelectrics considered by Samara the long-range forces in $\mathrm{LaP_5O_{14}}$ are (by symmetry) of quadrupolar nature ($m = 5$) and thus increase more rapidly with pressure than dipolar interactions ($m = 3$). As $\omega_\mathrm{h}^2 < 0$ we have $A < B$. Despite the higher value of m, if these two coefficients have approximatively the same magnitude, the pressure dependence of ω_h^2 is still the one predicted by Samara, and determining $dT_c/dp \leqslant 0$. However, a possibility of obtaining the opposite sign appears if $A << B$, with, as an extreme situation the case $A = 0$. We then have for this case

$$\frac{d\omega_\mathrm{h}^2}{dp} \approx -5\omega_\mathrm{h}^2 \frac{1}{r}\left(\frac{dr}{dp}\right) , \tag{10}$$

where $(1/r)(dr/dp)$ is the inverse of an elastic stiffness. We can evaluate this term since we know the elastic constants of $\mathrm{LaP_5O_{14}}$. On this basis, and using Eq. (7) we then obtain

$$\frac{dT_c}{dp} \approx +1 \text{ K/kbar} ,$$

still too small to account for the observed effect (with $A > 0$ the shift would even be smaller).

Another possible explanation of the considered anomalous behavior lies in the pressure dependence of the a coefficient. This coefficient determines the temperature dependence of the soft optic mode above T_c. Within experimental accuracy we have not detected any change in this slope with pressure. We can note, however, that to induce the required shift of T_c (42 K) between 1 bar and 2 kbar, a decrease of the slope of only 9% is needed. We obtain for instance a theoretical frequency at 200 °C and 2 kbar of 20.95 cm^{-1} while measurements indicate (21.15 ± 0.20) cm^{-1}. We cannot, therefore, rule out that the observed shift of T_c results from a change in the a coefficient. Such a circumstance would mean, as shown by Eq. (5) that by contrast to Samara's assumption, the anharmonic contribution to the pressure dependence cannot be ignored. Accurate measurements performed at higher pressures are needed to confirm this possibility. If they clearly demonstrate that a is in fact pressure independent, this would cast a doubt on the universality of Samara's ideas. In particular, it would be necessary to reexamine the short-range and long-range contributions to the harmonic frequency considered in the formula (9).

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