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Pressure-induced phase transition in SrF_2: A Raman study

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Measurements of Raman scattering under hydrostatic pressure in SrF_2 show that the $\beta\rightarrow\alpha$ phase transition, common to fluorite structures, occurs around 5.0 GPa at 300 K. Symmetry assignment of phonons in the α phase is based on a comparison to other fluorite crystals. Hysteresis phenomena are observed and discussed. Anharmonic processes are shown to be small but not negligible.

I. INTRODUCTION

Among the divalent fluorites with the general formula AX_2 there are several compounds which under high pressure can undergo a cubic-to-orthorhombic phase transition at 300 K. These are CaF_2, SrF_2, BaF_2, and PbF_2. Under normal conditions the above materials crystallize in the cubic fluorite structure which because of its relatively simple lattice has been extensively used in the past for testing fundamental models of lattice dynamics.[1] The same materials are also known to belong to the class of superionics, or fast-ion conductors, due to the anomalously high ionic conductivity they exhibit at high temperatures.[2]

The cubic-to-orthorhombic phase transition, commonly known as the $\beta\rightarrow\alpha$ transition, has been studied previously in BaF_2 and PbF_2 by use of Raman techniques.[3,4] To our knowledge no such studies have been reported for SrF_2 and CaF_2. The cubic-phase spectra under pressure of CaF_2 can be found in various places[3-6] while those of SrF_2 have been measured up to 10 kbar only.[6] Nonspectroscopic information about the transition pressure P_c of CaF_2 at 300 K has been reported by Jamieson and Dandekar,[7] who place it between 8 and 8.5 GPa. The corresponding information given by the latter authors about SrF_2 is rather vague.

In this article we present the results of Raman measurements for SrF_2 at 300 K for pressures ranging from zero to well above the transition point. New optical phonons corresponding to the α phase are observed above the transition pressure. Because of experimental limitations their symmetry could not be determined directly from polarized spectra. Instead, the symmetries were derived by comparison to those of $BaBr_2$. Symmetry assignments in this material are known from direct measurements.[8] The reverse phase transition $\alpha\rightarrow\beta$ was observed with decreasing pressure at a much lower transition pressure, thus revealing a hysteresis in the $\alpha\rightarrow\beta$ phase transition. From the spectra recorded throughout the entire range of increasing and decreasing pressures, we were able to study the pressure dependence of the phonon frequencies in both phases and determine the corresponding Grüneisen parameters. These results were then combined with existing variable temperature data in the cubic phase to obtain information about the lattice anharmonicity of the material.

II. EXPERIMENTAL RESULTS

The Raman spectra were recorded using a Spex double monochromator operating with holographically ruled gratings. The instrumental bandpass was 2.8 cm^{-1}. An RCA model No. 31034 cooled photomultiplier and a photon-counting detection system were used along with a LeCroy 3500 multichannel analyzer. For excitation the 514.5-nm line of an Ar^+ laser was employed in the backscattering geometry. The power level was about 500 mW. A gasketed diamond anvil cell was used to generate the hydrostatic pressure.[9] The well-known ruby-fluorescence technique was used to determine the pressure in the sample chamber.[10] For the room-temperature measurements the standard 4:1 methanol-ethanol mixture was used as the pressure-transmitting medium. The low-temperature (35 K) measurements were carried out at the Max-Planck-Institut, Stuttgart, using a flowing-liquid-helium cryostat and solid argon as the pressure-transmitting medium.[11]

The crystals were obtained from Harshaw Chemical Company. The sample chips used were randomly oriented, so that no polarization measurements were possible.

In its cubic (β) phase (space group O_h^5 or $Fm3m$), SrF_2 exhibits only one triply degenerate $q\approx 0$ optical phonon (symmetry F_{2g}), which is Raman active and ir inactive. In Fig. 1 we show the Stokes spectra of this phonon for $P=0$ and 4.4 GPa (a and b, respectively). At a pressure of 5.0 GPa the spectrum shows a drastic change (c). We attribute this change to the $\beta\rightarrow\alpha$ phase transition, where α is the orthorhombic phase (space group D_{2h}^{16} or $Pnma$). Based on such repeated measurements, the transition point is placed at $P_c=5.0\pm0.2$ GPa. The spectrum in the α phase is characterized by additional peaks corresponding to new Raman-active phonons. A general reduction of the scattering intensity is also observed when comparing the main peaks of spectra a, b, and c. Physically, the orthorhombic phase is formed because the cations are displaced in equal numbers upward and downward from their former (111) planes to adjacent nonequivalent (111) anion planes.[8]

The highest pressure applied was 6.8 GPa (spectrum d). As the pressure was gradually released, the spectra retained the same structure even well below P_c (e). At about 1.4 GPa and lower, the spectrum recovered its zero pressure form, that is the single peak (*f*) which characterizes the cubic phase. Repeating the cycle by increasing the pressure from 0 through 1.4 GPa did not alter the one-peak spectrum except for its frequency shift, as expected. Only after the pressure reached and exceeded the transition point P_c, did the spectrum reveal once more the $\beta \rightarrow \alpha$ phase transition.

In summary, the $\beta \rightarrow \alpha$ phase transition of SrF_2 occurs at $P_c = 5.0 \pm 0.2$ GPa and is a reversible transition. The reverse transition $\alpha \rightarrow \beta$ exhibits an hysteresis and occurs at $P_c' = 1.7 \pm 0.2$ GPa. The $\beta \rightarrow \alpha$ phase transition in SrF_2 has been observed previously by *in situ* x-ray diffraction measurements.[7] The corresponding reduction of volume has been determined as 8%. However, the level of accuracy in these studies did not allow determination of P_c. Moreover, it was stated in Ref. 7 that the phase was irreversible even at atmospheric pressure (i.e., $P_c' = 0$). This is contrary to the present observations ($P_c' = 1.7$ GPa); it should be noted, however, that the experimental conditions in Ref. 7 were totally different. Similar hysteresis phenomena have been seen and studied in BaF_2, based on measurements of the static dielectric constant under pressure.[12] The $\beta \rightarrow \alpha$ transition in PbF_2 is not even reversible.[12] At this point it should be mentioned that, according to our preliminary experiments[13] in CaF_2, the $\beta \rightarrow \alpha$ transition occurs at about 8.5 GPa, in agreement with Ref. 7. However, the experimental conditions were not favorable enough to determine unambiguously the frequencies of the phonons in the α phase or to look for a hysteresis in the $\alpha \rightarrow \beta$ phase transition.[13] More work in CaF_2 is now in progress.

Symmetry analysis shows that with 12 atoms per unit cell in the α phase, as many as 18 Raman-active modes $(6A_g + 6B_{1g} + 3B_{2g} + 3B_{3g})$ should be expected.[14] The total number of phonons observed in the α phase of SrF_2 is six, those shown in Fig. 1. Limited resolution and low signal levels prevented us from identifying all 18 modes expected. An attempt to improve the quality of the spectra by lowering the temperature to 35 K showed that the phase transition did not occur for pressures up to 8 GPa. In fact at about 7.5 GPa the sample acquired a permanent milky appearance and the spectrum deteriorated quickly. These observations indicate that P_c, the transition pressure, is strongly dependent on temperature.

In both phases, the frequencies of the major phonon peaks were measured as a function of increasing and decreasing pressures at 300 K. The results are shown in Fig. 2. In the same figure the data at 35 K are included. Notice that the F_{2g} phonon of the cubic phase evolves to a phonon or cluster of unresolved phonons in the α phase. Their lumped frequency varies with pressure at the same

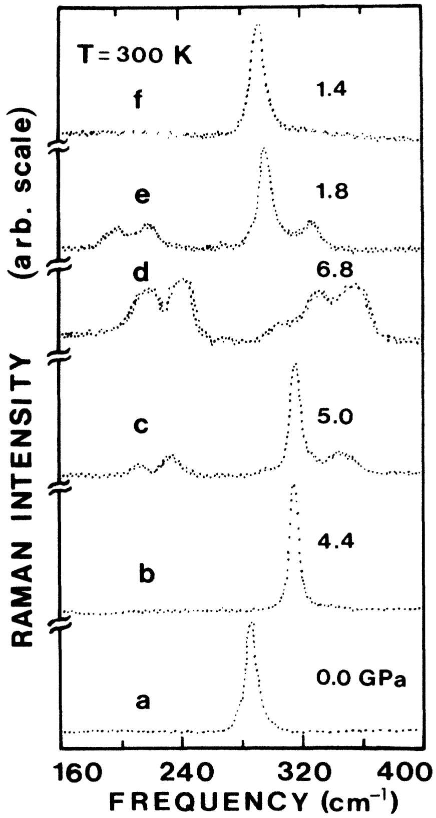

FIG. 1. Raman spectra of SrF_2 at 300 K under variable hydrostatic pressure. Spectra (*a*) and (*b*) are from the cubic phase. Spectrum (*c*) at 5 GPa is already from the orthorhombic phase, as is spectrum (*d*). Spectra (*e*) and (*f*), taken with decreasing pressure, confirm the hysteresis in the $\alpha \rightarrow \beta$ phase transition. Laser wavelength and power were 514.5 nm and 500 mW, respectively. Incident radiation was polarized; scattered radiation was unpolarized.

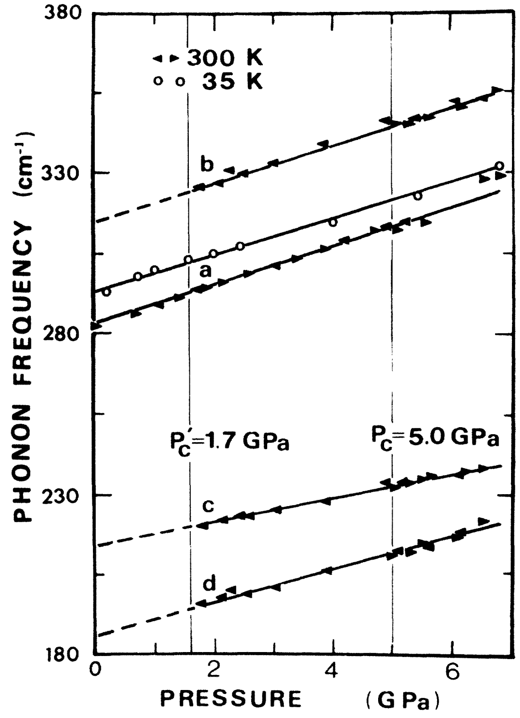

FIG. 2. Pressure dependence of phonon frequencies in the cubic phase at 300 and 35 K, (*a*), and in the orthorhombic phase at 300 K, (*b*)–(*d*). The triangular points are so oriented as to indicate the direction of pressure variation: Solid lines are best fits and dashed lines are extrapolations to zero pressures. Other details as in Fig. 1.

TABLE I. Observed phonon frequencies of SrF_2 at 300 K and pressures 0 and $P_c = 5.0$ GPa. Symmetry assignments are included. The slopes B and the mode Grüneisen parameters are based on the best fits of Fig. 2, except for the 297- and 355-cm^{-1} phonons, for which an average value for B is used.

Phase	Symmetry	$\omega(0)$[a]	$\omega(P_c)$ (cm^{-1})	A (cm^{-1})	B (cm^{-1}/GPa)	γ^T
β	F_{2g}	286.0	317	286.0	6.18	1.51
					7.00[b]	1.60[b]
	A_g,B_{1g}	187.8	212	196	4.84	1.89
	A_g,B_{1g},B_{3g}	213.9	233	220.4	3.83	1.29
	A_g,B_{2g}	272[c]	297	280.5[c]	5[c]	1.33
α	B_{1g},B_{3g}	286	317	296.5	6.18	1.69
	A_g,B_{1g}	316	344	325.5	5.62	1.36
	B_{2g}	330.0[c]	355	338.5[c]	5[c]	1.06

[a] Measured value (β phase) or by extrapolation (α phase).

[b] Reference 6.

[c] Based on average $B = 5$ cm^{-1}/GPa.

rate as the F_{2g} phonon. The slopes $(\partial\omega/\partial P)_T$ at 300 K were determined from the data with a linear least-squares fitting procedure. The results are shown in Fig. 2 by solid lines which obey the following expressions,

$$\omega(P) = A + BP \ , \quad P \le P_c \text{ for the } \beta \text{ phase} \ , \tag{1}$$

$$\omega(P) = A + B(P - P_c') \ , \quad P \ge P_c' \text{ for the } \alpha \text{ phase} \ . \tag{2}$$

All pressures are in GPa and $P_c = 5.0$ and $P_c' = 1.7$. The values of A and B for the various modes are listed in Table I together with the frequencies of the phonons of both phases at $P = P_c$ (measured values) and $P = 0$ (measured value for the β phase, extrapolated values for the α phase).

All phonons will be labeled by their $\omega(p_c)$ value hereafter. The slopes B for the phonons at 297 and 355 cm^{-1} were not actually measured because of poor signal conditions at high pressures. The corresponding values of $\omega(0)$ and A were deduced from Eq. (2) with the use of $\omega(P_c)$ and a value of B equal to the average of all measured values. Finally we note that the slope for the F_{2g} phonon at 35 K is slightly lower (5.6 cm^{-1}/GPa) than that at 300 K. This will contribute somewhat to the temperature dependence of the mode Grüneisen parameter, without any further consequences as far as the present study is concerned. The rest of this work will therefore refer to our data at 300 K only.

III. SYMMETRY ANALYSIS

The second column of Table I includes the tentative symmetry assignments of the modes observed. They are based on a comparison of the present spectra with those of $BaBr_2$, BaF_2, and PbF_2 for which such assignments are available.[4,8] (Application of polarization selection rules was not possible in the present study because of the small size of the SrF_2 sample inside the diamond anvil cell). In comparing SrF_2 with BaF_2 and PbF_2 we have assumed that for those modes which involve purely motion of the cation, the corresponding frequencies scale as the inverse square root of the cation atomic weight. There are six such modes, with frequencies in the low region of the spectrum and symmetries $2A_g$, $2B_{1g}$, B_{2g} and B_{3g}.[4,8,14] Upon scaling the six frequencies of PbF_2 (BaF_2) tabulated in Ref. 4, we find that the corresponding low-lying frequencies of SrF_2 at 300 K should be lower than about 120 (110) cm^{-1}. In our experiments, under high pressure, no scattering activity was observed in the range below 180 cm^{-1}. We conclude that the low-frequency part of the spectrum in SrF_2 is overly weak to be observed at 300 K.

The middle-frequency range of the spectra in PbF_2, BaF_2, and $BaBr_2$ includes two sets of modes each. These are (A_g,B_{1g}) and (A_g,B_{1g},B_{3g}) and involve motion of both cations and anions. Since SrF_2 has the same anion as PbF_2 and BaF_2 we tend to use the same scaling argument as above. The results show that the two sets of SrF_2 should appear in the ranges 150—203 cm^{-1} and 217—267 cm^{-1}, respectively. The spectrum of Fig. 1 shows that the peaks at 212 and 233 cm^{-1} may reasonably be assigned to two clusters of unresolved modes with symmetries (A_g,B_{1g}) and (A_{1g},B_{1g},B_{3g}), respectively (Table I). No further resolution was possible at 300 K.

The high-frequency part of the spectra in PbF_2, BaF_2, and $BaBr_2$ includes four sets of modes each. These are (A_g,B_{2g}), (B_{1g},B_{3g}), B_{2g}, and (A_g,B_{1g}) and involve motion of the anions only. It would be reasonable therefore to scale the $SrBr_2$ frequencies according to the anion atomic weight. Since no information is available about $SrBr_2$ we use the high frequencies of $BaBr_2$ given in Refs. 4 and 8 and scale them according to the anion as well as the cation atomic weight. The results show that the four sets above should appear around the values 294, 322, 348, and 343 cm^{-1}, respectively. These frequencies match very well those of Fig. 1 at 297, 317, 355, and 344 cm^{-1}. Thus we assign them to clusters of unresolved modes with symmetries (A_g,B_{2g}), (B_{1g},B_{3g}), B_{2g}, and (A_g,B_{1g}), respectively (Table I). Notice in particular that the F_{2g} phonon of the β phase evolves to the double phonon (B_{1g},B_{3g}) in the α phase. In keeping with the analogy to $BaBr_2$ and BaF_2, it could be stated that most of the scattering intensity originates from the B_{2g} component.

This completes the present partial symmetry assignment based on semiempirical arguments and the only known experimentally verified assignments in $BaBr_2$.[8]

TABLE II. Physical parameters and results of calculations for alkaline-earth fluorites. All entries refer to 300 K.

	CaF_2	SrF_2	BaF_2
β $(10^{-5}K^{-1})^a$	5.70	5.45	5.60
κ $(10^{-2}GPa^{-1})^a$	1.22	1.43	1.77
$\left[\frac{\partial\omega}{\partial T}\right]_P$ $(10^{-2}cm^{-1}K^{-1})^b$	−2.47	−1.94	−1.86
$\omega_{F_{2g}}$ (cm^{-1})	322^b	286	241^b
	329.5^c	292^c	246.5^c
$\left[\frac{\partial\omega}{\partial P}\right]_T$ $(cm^{-1}GPa^{-1})^c$	7.4^d	6.2	8.5^d
γ^T	1.88	1.51	2.00
γ^P	1.34	1.24	1.38
γ^V	−0.54	−0.27	−0.62
$\left[\frac{\partial\omega}{\partial T}\right]_V$ $(10^{-2}cm^{-1}K^{-1})$	0.99	0.42	0.82
$\Delta\omega_{tot}$ $(cm^{-1})^b$	−7.4	−5.8	−5.6
$\Delta\omega_{vol}$ $(cm^{-1})^b$	−10.2	−7.6	−8.1
$\Delta\omega_{anh}$ (cm^{-1})	2.8	1.8	2.5
η	1.40	1.22	1.44

[a] Reference 12.

[b] Reference 17.

[c] Extrapolated values to zero temperature.

[d] Reference 3.

IV. ANHARMONICITY STUDY

The mode Grüneisen parameters under constant temperature (300 K) for the phonons observed in both phases are listed in Table I. Their calculation was based on the slopes B, the zero-pressure frequencies $\omega(0)$ (measured or by extrapolation), and the definition

$$\gamma^T=\frac{1}{\kappa\omega(0)}\left[\frac{\partial\omega}{\partial P}\right]_T , \tag{3}$$

where κ is the isothermal compressibility. The parameter γ^T represents the volume effect on ω and its value for the F_{2g} phonon in the β phase is comparable to the value found in the literature.[6] Basically the same value has been obtained recently from independent Raman experiments under uniaxial stress.[15] This value will be used next to assess the level of anharmonicity between the F_{2g} mode and the cubic lattice. (No such study can be undertaken for the phonons in the α phase because their temperature dependence is not known).

One starts with the following relation:[16]

$$\gamma^P=\gamma^T+\gamma^V , \tag{4}$$

where

$$\gamma^P=-\frac{1}{\beta\omega(0)}\left[\frac{\partial\omega}{\partial T}\right]_P , \tag{5}$$

and

$$\gamma^V=-\frac{1}{\beta\omega(0)}\left[\frac{\partial\omega}{\partial T}\right]_V , \tag{6}$$

and β is the volume thermal expansion coefficient at 300 K. γ^P and γ^V correspond to mode Grüneisen parameters under constant pressure and constant volume, respectively. The parameter γ^P represents the total effect of temperature on ω and includes contributions from volume expansion (γ^T) and anharmonicity (γ^V). Mead and Wilkinson[17] have established the value of -1.94×10^{-2} cm^{-1}/K for the slope $(\partial\omega/\partial T)_P$, from which we obtain $\gamma^P=1.24$ and, using Eqs. (4) and (6), $\gamma^V=-0.27$ and $(\partial\omega/\partial T)_V=0.42\times10^{-2}$cm^{-1}/K. These and the corresponding calculated values for CaF_2 and BaF_2 are listed in Table II together with other necessary crystal parameters.

Comparison of the values and signs of γ^V and γ^T for the three materials leads to the conclusion that the total downward shift of ω with increasing T consists of a downward shift due to volume expansion and a smaller upward shift due to anharmonicity. More quantitatively, one can write for the observed total shift of ω with increasing T,

$$\omega(T)-\omega(T=0)=\Delta\omega_{tot}=\Delta\omega_{vol}+\Delta\omega_{anh} . \tag{7}$$

The total shift $\Delta\omega_{tot}$ is directly read or computed (Fig. 4 or Table I or Ref. 17). So is the volume contribution $\Delta\omega_{vol}$ (Fig. 6 of Ref. 17). These values for $T=300$ K and the term $\Delta\omega_{anh}$ are included in Table II. It turns out that for all three materials the volume contribution prevails over anharmonicity. The latter is mainly due to three-phonon processes[16,17] and causes a positive shift of the phonon frequency. This conclusion is the same as that reached in Ref. 17 for BaF_2 and CaF_2, but opposite to that implied for SrF_2. However, the conclusion reached in Ref. 17 for SrF_2 does not seem to be consistent with the data shown in the same reference. Finally, from the values of γ^P and γ^T we calculate the implicit fraction $\eta=\gamma^T/\gamma^P$. The values for all three materials are larger than 1 and comparable in size. According to the general scheme of Weinstein and Zallen,[18] such values imply ionic bonding for the moving ions which, for the phonon under consideration (F_{2g}), are the fluorine anions. It is noted that the same behavior was recently observed in LaF_3 for those optical phonons which involve motion of fluorine anions.[16] It was concluded there that the bonding of fluorine ions is ionic and that the level of anharmonicity for the same phonons is rather low. In this regard it would be interesting to study under variable temperature the frequency of those phonons in SrF_2 which involve motion of the cations. Such are the $q\approx0$ optical phonons of F_{1u} symmetry in the cubic phase. These experiments require infrared spectroscopic techniques, since the F_{1u} phonons are ir active and Raman inactive. Although variable pressure experiments can be found in literature at least for the transverse component of the F_{1u} phonons,[5] to our knowledge no measurements under variable temperature have been reported whatsoever.

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