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Temperature and pressure dependence of the Raman spectrum of crystalline P_4S_3

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The Raman spectrum of P_4S_3 has been investigated as a function of temperature (10 to 320 K) at ambient pressure and as a function of hydrostatic pressure to 86 kbars at room temperature. External and internal mode frequencies have been identified by studying the spectrum in solution and by observing pressure-induced changes in the spectrum. The external modes, which are believed to be due to the librational motion of the molecules in the crystal, disappear completely at the crystalline-plastic phase transition near 314 K, leaving only a wing to the Rayleigh scattered component. From this result it is concluded that the P_4S_3 molecules gain rotational freedom in the high-temperature plastic β phase. The external mode frequencies are particularly strongly pressure dependent whereas the internal mode frequencies are affected to a lesser extent by pressure. The low-temperature spectrum reveals crystal-field and Davydov splitting because of line narrowing, while pressure enhances these splittings because of stronger intermolecular interaction resulting from compression. The external mode spectrum is richer at high pressure due to increased resolution resulting from a selective pressure effect on the external mode frequencies. The $d\nu/dP$ data are analyzed in terms of the scaling law for the Grüneisen parameter proposed by Zallen. The volume and the phonon excitation contributions to $d\nu/dT$ are analyzed.

I. INTRODUCTION

The Raman spectra of complex molecular crystals exhibit a wealth of details in which the internal modes representing the intramolecular vibrations are often well separated from the external modes arising out of the intermolecular vibrations. When a phase change occurs in these systems the external modes may be expected to undergo dramatic changes, while the internal modes are expected to remain unaffected. Also, since this class of crystals undergoes a large compression even at moderate pressures, the external modes exhibit a strong pressure dependence while the internal modes shift only weakly with pressure. The above is also generally true for their temperature sensitivity. Hence much can be learned about the intermolecular forces operative in these systems from pressure- and temperature-dependent Raman scattering studies. Despite this fact, there have not been many pressure studies on molecular crystals and only a very few are reported for inorganic molecular crystals.[1-3] The usefulness of such a study has recently been demonstrated by Zallen and Slade[2] who have carried out a rather extensive pressure and temperature investigation on As_4S_4 and S_4N_4, from room temperature to 10 K and to pressures of 40 kbars using the diamond anvil apparatus. This classic study may be said to be a pace setter. Although no phase transitions were encountered, the effect of crystalline field, the Davydov splittings, and scaling behavior of the mode Grüneisen parameters have been clearly revealed and discussed.

Our interest in α-P_4S_3, which forms a molecular crystal, was initially stimulated by the so-called crystalline-to-plastic phase transition ($\alpha \rightarrow \beta$ transition) near 314 K (Ref. 4), believed to be due to orientational disordering of the molecules still occupying the lattice sites in the crystal. However, the center-of-gravity structure of the β phase is different from that of the α phase. We felt that the above mentioned crystalline-to-plastic transition can be understood at a microscopic level through a Raman scattering study of crystalline P_4S_3 as a function of temperature. Also, we undertook a high-pressure study in the hope of obtaining information on intermolecular forces, crystal-field-induced changes of the vibrational modes and the possible approach to the breakdown of the "molecular crystal approximation."

Previous Raman and infrared studies on P_4S_3 (Refs. 5 and 6) have shown that the P_4S_3 molecules remain practically unchanged in its various states of aggregation, as well as in solution. But these studies have been mainly on the internal mode behavior. Suprisingly, the earlier Raman studies have failed to observe the low-frequency external modes. In the present study we have observed them and have followed them as a function of pressure from ambient pressure to nearly 86-kbar pressure and as a function of temperature to their disappearance at the $\alpha \rightarrow \beta$ transition (314 K). From the large pressure dependence of the low-frequency spectrum we were able to confirm their origin as external modes. The latter modes disappear at the crystalline-to-plastic phase transition. We interpret this as due to a gain in the rotational freedom of the molecules, which in the high-temperature phase are able to rotate almost freely and isotropically, with the center of gravity of the molecules still occupying the lattice sites in the high-temperature β phase. Pressure and low-temperature spectra exhibit shifts and splittings which we associate with crystal-field effects and Davydov splitting. We have also attempted to test the validity of the vibrational scaling law proposed by Zallen,[1] using our pressure data on P_4S_3. These experiments and the results will be presented and discussed in this paper.

II. VIBRATIONAL ANALYSIS

A. Molecular and crystal structure

The molecular compound α-P_4S_3 crystallizes[7,8] in the orthorhombic space group $Pmnb(D_{2h}^{16})$ with $a = 9.670(3)$, $b = 10.599(4)$, and $c = 13.678(3)$ Å at 293 K. There are eight molecules in the unit cell. The molecule has an almost spherical cagelike structure with C_{3v} point-group symmetry (Fig. 1). In the crystal the molecules retain only one symmetry plane. Figure 2 shows the projection of the crystal structure along the [100] direction. There are two independent molecules in the asymmetric unit and the molecules arrange themselves in two sets. There is no symmetry operation relating these two sets. The mirror planes of the molecules lie on the mirror planes of the crystal at heights $x = \frac{1}{4}$ and $\frac{3}{4}$. It can easily be seen that the molecules are packed approximately in hexagonal-closed-packed arrangement. The pseudohexagonal cell with two molecules per cell is outlined in Fig. 2.

B. Symmetry analysis

The symmetry types and selection rules for the vibrational normal modes of an isolated P_4S_3 molecule are directly obtained by the reduction of 21-dimensional representation Γ_{mol}, generated by the atomic displacements, into irreducible representations of the C_{3v} point group:

$$\Gamma_{\text{mol}} = 5A_1 + 2A_2 + 7E \ . \qquad (1)$$

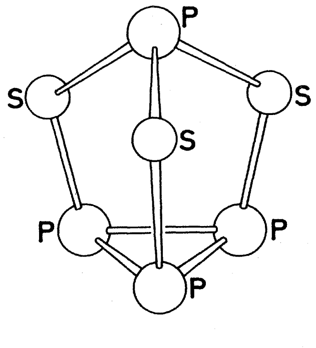

FIG. 1. Cagelike molecule P_4S_3. The smaller spheres are the sulfur atoms and the larger ones are the phosphorus atoms.

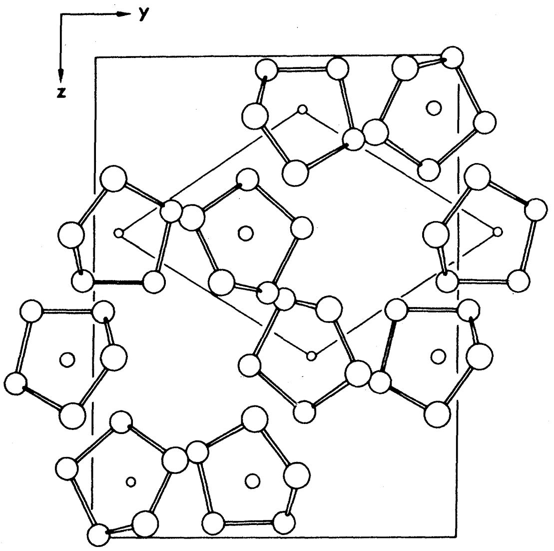

FIG. 2. Projection of the structure of α-P_4S_3 crystal along the [100] direction. The pseudohexagonal cell is indicated. The molecules are packed approximately in hexagonal-closed-packed arrangement. The centers of gravity of the molecules are indicated by small and large circles. Smaller circles lie at $x = \frac{1}{4}$ whereas larger ones lie at $x = \frac{3}{4}$.

For the intramolecular or internal modes, we subtract the rigid translations ($T = A_1 + E$) and rotations ($R = A_2 + E$) which lie at zero frequency for the free molecule:

$$\Gamma_{\text{mol}}^{\text{int}} = 4A_1 + A_2 + 5E \ . \qquad (2)$$

Both A_1 and E modes are Raman and infrared active whereas the A_2 mode is inactive in both. There are therefore nine Raman and infrared-active eigenfrequencies for the isolated molecule.

In the crystal, the vibrations which directly couple to light via first-order Raman scattering or infrared absorption are the zone-center ($q = 0$) optical phonons. Considering the eight seven-atom molecules in the unit cell belonging to space group D_{2h}^{16}, the 168-dimensional representation is too complex. A better understanding is gained by considering the eight molecules in the cell to be rigid units, having three translational and three rotational degrees of freedom. These degrees of freedom of the rigid units give rise to the external modes. The 24-dimensional representation $\Gamma_{\text{trans}}^{\text{ext}}$ for translational degrees of freedom can be reduced after subtracting the three acoustic modes ($B_{1u} + B_{2u} + B_{3u}$),

$$\Gamma_{\text{trans}}^{\text{ext}} = 4A_g + 2B_{1g} + 2B_{2g} + 4B_{3g} + 2A_u + 3B_{1u} + 3B_{2u} + B_{3u} \ . \qquad (3)$$

Similarly for rotational degrees of freedom the

24-dimensional representation $\Gamma_{\rm rot}^{\rm ext}$ can be reduced to

$$\Gamma_{\rm rot}^{\rm ext} = 4A_g + 2B_{1g} + 2B_{2g} + 4B_{3g} + 2A_u + 4B_{1u} + 4B_{2u} + 2B_{3u} \,. \qquad (4)$$

Figure 3 schematically displays the relationship between the vibrational spectra of the free molecule and of the weakly coupled molecular crystal. Vibrational eigenfrequencies are represented by levels which are placed so as to elucidate the molecular origin of the zone-center crystal modes. Intermolecular interaction effects are treated as small perturbations. Each of the four nondegenerate internal A_1 modes gives rise to a closely spaced $A_g + B_{1g} + B_{2g} + B_{3g} + A_u + B_{1u} + B_{2u} + B_{3u}$ Davydov octet. In this case a Raman quartet is expected because the four components of even parity (*gerade*) are Raman active. Similarly, since B_u modes are infrared active an infrared triplet is predicted. There is an inactive A_u mode. Although the molecular Raman and the infrared-inactive A_2 mode is allowed in the crystal and is expected to give rise similarly to a Raman quartet, an infrared triplet and an inactive mode, we may expect these lines to be very weak since these vibrations are forbidden for the free molecule.

Each of the five doubly degenerate E modes will give rise to 16 closely spaced lines rather than octets. This may be understood in the following way. When the molecules are placed in the crystal they do not retain their full C_3 symmetry but have the point-group symmetry C_s. This will remove the degeneracy of each of the E doublet. The crystal-field splitting is the same for each molecule. Now the coupling between the eight identical oscillators in the unit cell will give rise to a Davydov octet.[9] Thus each of the five E modes should give rise to a Raman octet plus six closely spaced infrared-active modes and two inactive A_u modes. At the bottom of Fig. 3 the genesis of the lattice or external modes are shown. The six zero-frequency modes of the free molecule $A_1 + A_2 + 2E$, namely the rigid translation and the rotation, give rise to $6\times 8 = 48$ external modes, of which three are acoustic modes and have zero frequency at $q = 0$. Therefore the 45 remaining modes constitute the external mode. Twenty four of these should be Raman active whereas 17 will be infrared active and four inactive modes.

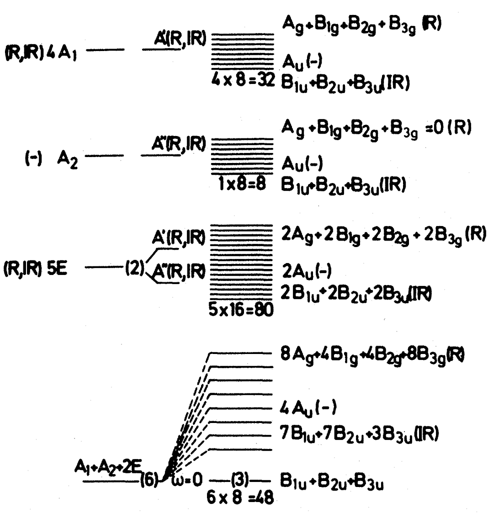

FIG. 3. Splitting of the molecular vibrational modes (internal modes) of P_4S_3 in the crystal and further splittings of the internal modes due to intermolecular interaction (Davydov splitting). The Raman activity is indicated by *R* and infrared activity by IR. A dash (—) means inactive mode. The lowest part of the diagram shows the crystal modes (external modes) and their activity.

III. EXPERIMENTAL

Commercial P_4S_3 was purified by recrystallization in CS_2 under nitrogen atmosphere. From the purified material single crystals up to a few cm in linear dimensions were grown from CS_2 solution. The crystals were transparent and yellow in color and could be cleaved easily. They were tested by x-ray precession technique to ensure the right crystal symmetry and the lattice constants. Crystals $2\times 3\times 3$ mm^3 in size were employed in Raman measurements at ambient pressure. For Raman studies at high pressure a gasketed diamond anvil cell was used in the back scattering geometry. An Inconel gasket 120 μm thick with a 200-μm aperture served as the pressure chamber.[10] This was filled with a 4:1 methanol-ethanol mixture to serve as the pressure medium. The sample of about 50 μm in linear dimensions and of about 40 μm in thickness was placed in the cell along with a tiny ruby chip. The latter served to measure the pressure generated by the well-known ruby fluorescence technique. All high-pressure Raman measurements were carried out at room temperature. For temperature-dependence studies, a cryostat provided with optical windows was used. The sample was cemented to a copper block located inside the cryostat. The block was heated electrically with a resistance element so that any desired temperature in the range 100 to 400 K could be obtained. Temperature was measured by a copper Constantan thermocouple placed close to the sample on the copper block.

Some of the Raman spectra were recorded using a Spex 1402 double monochromator (wave-number calibration) and others using a Spex 1401 double monochromator (wavelength calibration) both instruments equipped with an RCA C 31034 photomultiplier cooled to −20 °C and conventional photon-counting system. Most of the experiments were performed with 6764-Å line of the krypton and the 5145-Å line of the argon laser were also used. To avoid laser heating of the samples, the power was limited to 20 mW when using the red lines and 2 mW when using the green line.

IV. TEMPERATURE DEPENDENCE OF THE RAMAN SPECTRUM

In Fig. 4 the Raman spectrum of crystalline P_4S_3 taken at 293 K is shown. It is clear that a well-defined gap exists between the low-frequency group of lines and the higher-lying frequencies (above 185 cm^{-1}). The lowest-frequency grouping originates from the external crystalline modes (intermolecular) while the higher-frequency grouping from the internal molecular modes (intramolecular). The observed frequency shifts are listed in Table I. The internal modes have been assigned in the earlier studies.[6] However, there are discrepancies between our results and previous measurements. We do not observe either the 145-cm^{-1} or the 373-cm^{-1} peak. Likewise we did not observe the overtones and combinations reported by Gardner.[6] The spectra become stronger and sharper at low temperatures, suggesting that the Raman peaks are first order. Surprisingly, the room-temperature low-frequency lines at 28, 36, 46, 59, and 72 cm^{-1} were not observed in previous studies.[5,6]

In Fig. 5 we compare the Raman spectrum of crystalline P_4S_3 taken near 320 K with the spectrum taken at room temperature (293 K), and also with the solution spectrum of P_4S_3 in CS_2. The purpose of the comparison of the latter with the crystal spectrum at 293 K is to confirm the origin of the lowest-frequency group, namely, that they are the external modes. Coming to the high-temperature spectrum (320 K), the remarkable feature is the disappearance of the external modes. In fact the spectrum is strikingly similar to the solution spectrum. The disappearance of the external modes must undoubtedly be due to the phase transition and we identify this with the so-called crystalline-to-plastic phase transition[4] discussed in detail later in the paper.

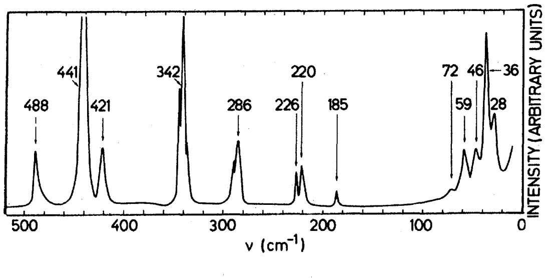

FIG. 4. Raman spectrum of α-P_4S_3 recorded at 293 K showing both the external (low-frequency part) and the internal modes. The number above the peaks indicate the wave-number shift in cm^{-1}.

In Fig. 6 we present the spectrum taken near liquid-He temperature, estimated to be about 10 K, along with the spectrum at 293 K. We have also recorded the spectrum near liquid-N_2 temperature, estimated to be 90 K which is also shown in the Fig. 6. In Table I the internal mode frequencies at 293 ~ 90, and ~10 K are listed. According to the enumeration of the Raman-active modes for the P_4S_3 crystal mentioned earlier, 60 crystal-field and Davydov split Raman-active frequencies are to be expected in the internal mode manifold. At room temperature these splittings are masked by the excessive linewidths; only a group of eight peaks are observed. At low temperature the lines sharpen and reveal the splitting, but even at 10 K not all the components are resolvable and we can observe only 26 of them. Again, the external mode peaks exhibit marked sharpening at low temperature and somewhat more structure is revealed. The observed frequency shifts in the external mode region are listed in Table I for 293, ~90, and ~10 K.

V. INFLUENCE OF PRESSURE

The pressure dependence of the Raman peaks is illustrated in Fig. 7 and the observed frequencies are plotted as a function of pressure in Figs. 8 and 9. It is evident from the latter figures that the external modes are strongly pressure sensitive compared to the internal modes. In fact it is this large difference in the pressure sensitivity which confirms the expectations that the low-lying group of lines must originate from the external modes. From group-theroretical analysis 24 Raman components are expected in the external mode region, whereas only five Raman peaks are actually observed at ambient pressure. However, at high pressure more of them are seen. For instance, at 76 kbars, 14 Raman components are seen in the external mode region. In this connection it is to be noted that (see the external mode region in Fig. 8) the higher-lying frequencies are seen to be more pressure sensitive compared to the lower-lying ones. It is this difference in response to pressure that spreads out the spectrum at high pressure and enables the observation of more peaks. The high-pressure spectrum may be expected to sharpen at low temperature and

TABLE I. Temperature dependence of phonon frequencies of external and internal modes of crystalline α-P_4S_3.

		Phonon frequency (cm^{-1}) at ambient pressure				
Type	Assignment	Gardner 293 K	Present work 293 K	Present 90 K	Present 10 K	$-\frac{d\nu}{dT}$ $\mathrm{cm}^{-1}/\mathrm{K}$
External modes			27.8	28.7	28.8	0.07
					33.8	
					36.4	
			36.2	38.4	39.8	0.13
					42.1	
					45.0	
					50.2	
			46.0	51.5	54.7	0.31
					63.0	
			58.5	63.5	67.7	0.30
					69.4	
			72.0	79.0	81.9	0.38
Internal modes	A_1	187	185.2	185.8	186.8	
	E	220	220.0	218.2	219.3	
				221.5	223.2	
	E	227	226.2	228.2	229.0	
					230.7	
					231.6	
	E	288	285.8	287.7	284.4	
					287.9	
					291.3	
					295.2	
	E	343	342.0		335.2	
			broad	338	337.6	
					341.7	
				343.3	344.0	
		347		347.2	348.6	
Internal modes	A_1	422	421.0	423.8	421.2	
					424.6	
					426.8	
	A_1				440.4	
		443	441.3	442.8	442.6	
					445.5	
					447.1	
	A_1+E				481.9	
		489	487.8		485.3	
				491.2	490.9	
					493.1	

reveal even more structure. In Table II the high-pressure Raman data are listed. In the last column of the table, the experimentally determined slopes $d\nu/dP$ are given. The pressure-induced shifts are found to be readily reversible.

In the internal mode region (see Fig. 8) eight branches of Raman-shifted components could be recognized and their pressure sensitivity varies from positive to negative $d\nu/dP$, with some components showing hardly any sensitivity. It can be said in general that the lower-frequency components in each branch are less sensitive to pressure than the upper-lying ones. This feature results in a pressure-induced higher spectral resolution, as in the case of the external mode spectrum. Consequently the high-pressure spectra reveal more structure, analogous to the low-temperature spectrum. In Fig. 10 we compare the high-pressure spectrum at 32 kbars with the 10-K spectrum. Except for shifts in the frequency of

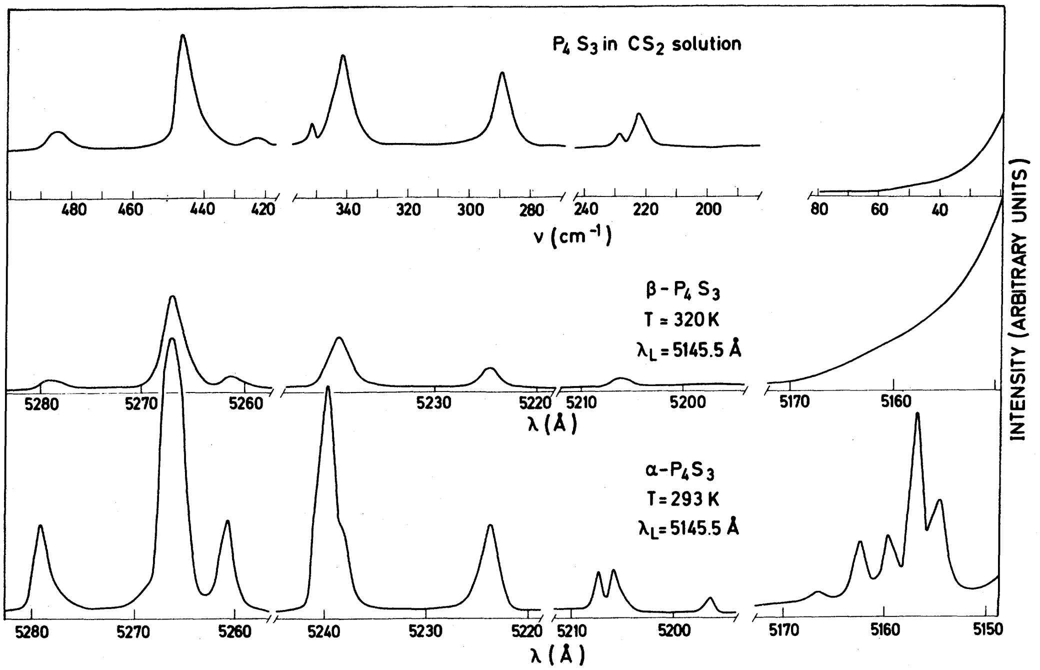

FIG. 5. Raman spectrum of α-P_4S_3 at 293 and 320 K and of P_4S_3 in CS_2 solution. The disappearance of the external modes at 320 K is to be noted. The spectrum at 320 K is to be compared with that at 293 K on the one hand and with the solution spectrum on the other hand. The disappearance of the external modes at 320 K is due to the crystalline-plastic phase transition at 314 K (see text for explanation).

the peaks, there is a remarkable correspondence between the two spectra. We believe pressure reveals the crystal-field and Davydov split components by enhancing the intermolecular interactions, whereas the same features are revealed in the low-temperature spectra because of the sharpening of the spectral features. In Table III the frequencies observed at 32 and 86 kbars are given for comparison with the 10-K spectrum.

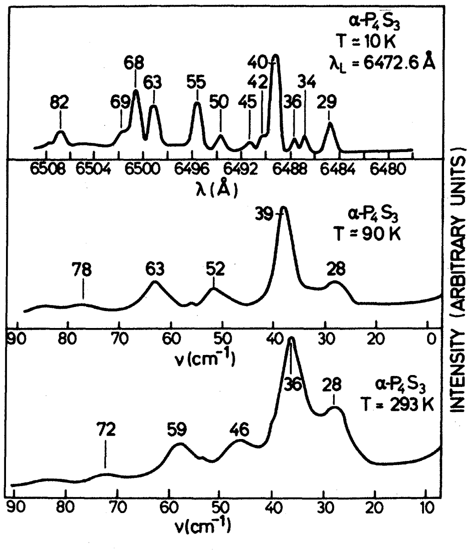

FIG. 6. Raman spectrum of α-P_4S_3 in the external mode region at 293, 90, and 10 K. Line narrowing and emergence of many more peaks are evident in the 10-K spectrum. The numbers above the peaks represent the frequeney shift in cm^{-1}.

We observe a contraction of about 20% in the size of P_4S_3 crystals in the 1- to 15-kbar range, when viewed in the optical cell. In analogy with the behavior of other molecular crystals the compression must be nonlinear, being initially large and decreasing at higher pressure. In fact the pressure effect on the external modes reflect this. It is seen from Fig. 8 that the major increase in the frequency of the external mode has already taken place between 0 and 35 kbars and the curves exhibit strikingly nonlinear pressure dependence. The pressure dependence of the internal modes on the contrary is nearly linear in the whole pressure range of this study. The principal effect of pressure may be said to result in stronger intermolecular interactions, while the effect on the intramolecular forces is much weaker. What is most surprising, however, is the observed softening of the two internal mode frequencies, which extrapolate to about 334 cm and 342 cm^{-1} at ambient pressure. Their pressure coefficients $d\nu/dP$ are −0.18 and −0.13 cm^{-1}/kbar. These two frequencies belong to the E modes. It is interesting to speculate on this behavior. Usually, mode

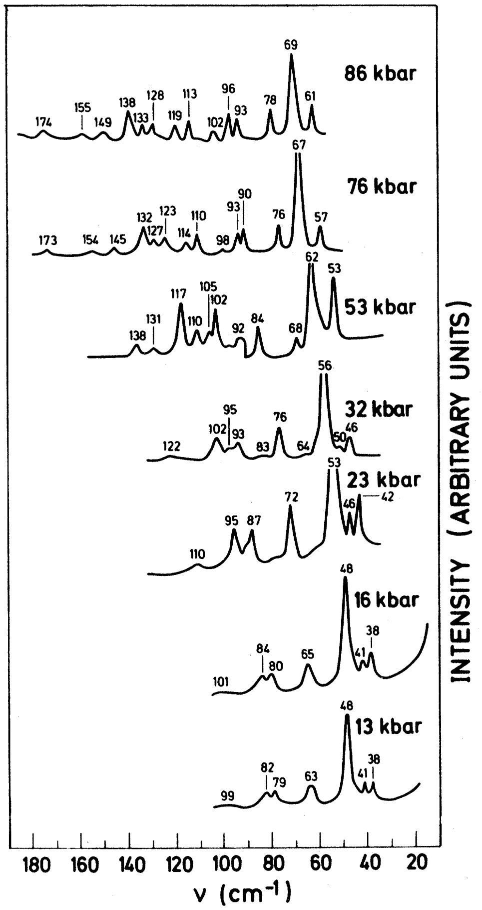

FIG. 7. Effect of pressure on the frequencies of α-P_4S_3 in the external mode region. At higher pressure the spectrum shows many more peaks. See text for explanation. The numbers above the peaks indicate the wave-number shift in cm^{-1}.

softening signifies a phase transition in the context of lattice modes. Examples of mode softening and their connection to phase transitions abound in literature.[11] Mode softening for an internal molecular vibration therefore, by analogy, may be thought of as an impending instability for the molecule. Whether it signifies an impending dissociation or other configurational changes is hard to decide, but softening of internal modes has to result in some change of state of the molecule.

VI. CRYSTALLINE-TO-PLASTIC PHASE TRANSITION

α-P_4S_3 is known to exhibit a first-order phase transition near 314 K to β phase which has been established by a variety of measurements: x-ray diffraction,[12] specific heat,[4,12] and NMR (Ref. 13). The highlight of the present study is that for the first time the changes in the Raman spectrum accompanying this transition have been observed. The presently observed external mode spectrum disappears at this so-called crystalline-to-plastic

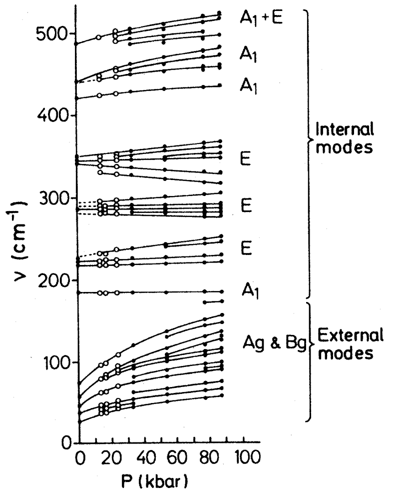

FIG. 8. Pressure dependence of the Raman frequencies. The external mode frequencies (lowest bunch of frequencies) are highly pressure sensitive. The internal mode region sorts itself into eight branches. The lowest branch at 180 cm^{-1} is pressure insensitive. All other frequencies increase with pressure except for the two which decrease. The hollow circles indicate experimental points obtained after releasing the pressure from 86 kbars.

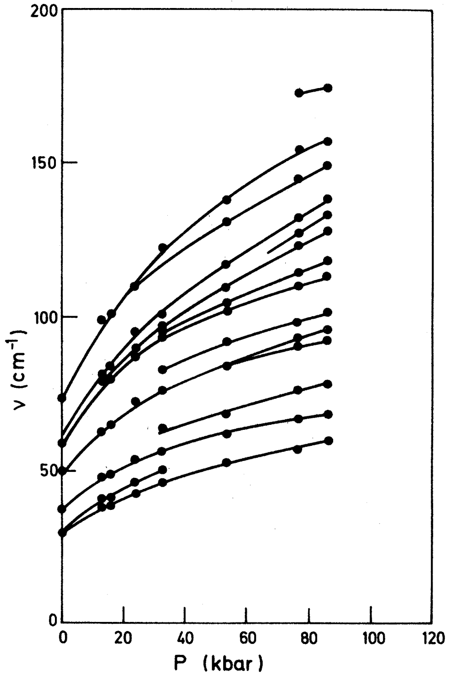

FIG. 9. Pressure effect on the external manifold (see Table II for the pressure coefficients).

TABLE II. Pressure dependence of phonon frequencies (cm^{-1}) of external and internal modes of crystalline α-P_4S_3 at 293 K.

Type	Assignment	Phonon frequency ν (cm^{-1})								$\left(\frac{d\nu}{dP}\right)$
		0 kbars	13 kbars	16 kbars	23.5 kbars	32.4 kbars	53.3 kbars	76.5 kbars	86 kbars	[cm^{-1}/kbar]
External modes		27.8	38	38	42	46	53	57	61	0.785
			41	41	46	50				1.015
		36.2	48	48	53	56	62	67	69	0.908
					61	64	68	76	78	
		46.0	63	65	72	76	84	90	93	1.308
								93	96	
						83	92	98	102	
			79	80	87	93	102	110	113	1.577
					90	95	105	114	119	
						97	110	123	128	
								127	133	
		58.5	82	84	95	102	117	132	138	1.769
							131	145	149	
		72.0	99	101	110	122	138	154	155	1.985
								173	174	
Internal modes	*E*	187	186	185	185	185	186	186	186	0.0385
	E	220	220	218	219	220	221	222	223	−0.0769
									227	
			224	224	225	227	229	231	232	0.2692
	E	227	234	234	238	241	242	245	248	0.6154
							245	252	254	
	E		282	282	281	282	280	278	278	−0.3077
							283	281	283	
							287	285	287	
		288	287	287	287	288	290	290	291	0.0769
			291	291	291	292	293	291	293	0.3846
								293	294	
			297	296	298	300	303	305	307	0.8462
	E		331		329	328	325	320	319	
		343	338		337	337	334	332	332	−0.3077
							347	348 + 350	351	
			343		345	347	351	354	355	0.0769
		347	347		350	352	358	362	364	0.3846
			351		354	358	363	367	369	
	A_1	422	425		427	430	433	435	437	0.2308

TABLE II. (*Continued*)

Type	Assignment	Phonon frequency ν (cm^{-1}) 0 kbars	13 kbars	16 kbars	23.5 kbars	32.4 kbars	53.3 kbars	76.5 kbars	86 kbars	$\left(\frac{d\nu}{dP}\right)$ [cm^{-1}/kbar]
Internal modes	A_1	443	444		447	450	454	456	458	0.1538
								459	461	
			449		455	456	464	472	475	0.5385
	A_1+E				457	460	471	479	483	
					490	484	489	493	497	0.0851
					491	491	497	502		0.1271
		488	496		498	501	507	513	517	0.4255
					501	504	512	520	524	0.5532

phase transition leaving a monotonically decreasing wing to the central component, which is probably related to the density of phonon states in the new phase (see Fig. 5). The internal modes are left intact and in fact the spectrum of the crystal at 320 K is strikingly similar to that of P_4S_3 molecule in solution. However, from x-ray diffraction studies on the β phase of P_4S_3, it is evident that there is long-range order for the center of gravity of the molecules above the transition temperature. The center-of-gravity structure of β-P_4S_3 is found to be a rhombohedral distortion of the cubic β-Mn structure.[14] The question is what happens at the transition.

In the α phase, P_4S_3 molecules librate about their mean position. The librational tensor of the P_4S_3 molecules has been determined from the rigid-body refinement of the x-ray diffraction data.[15] An average librational amplitude of 4–6 degrees has been obtained from an analysis of the x-ray data at 292 K. A rough estimate of the librational amplitude can be inferred from the Raman frequencies attributable to the external mode by using the expression due to Cruickshank,[16]

$$\overline{\phi^2} = 4050\frac{h}{\pi^4 I_\mu}\coth\frac{h\nu}{2kT}\ , \qquad (5)$$

where $\overline{\phi^2}$ is the mean-square librational amplitude in deg^2, h the Planck's constant, I the moment of inertia of the molecule about the librational axis, ν the frequency of libration, k the Boltzmann constant, and T the temperature. Using a value of $801.32\times10^{-40}\ \mathrm{g\,cm^2}$ for the moment of inertia about the threefold axis of the molecule, the librational amplitude corresponding to the low-frequency Raman lines 28, 36, 46, 58.5 cm^{-1} are 7.7, 5.9, 4.8, and 3.7 degrees, respectively, at $T = 293$ K. Thus the external mode frequencies are in the regions where the librational modes are expected. In the plastic phase (β phase) these modes disappear, which we interpret as due to a gain in the freedom of P_4S_3 molecules for rotation. The molecules either rotate freely and isotropically, or they execute large librations, sitting on several potential wells and continuously reorient themselves in these potential wells. Such a situation would wipe out the previously observed librational modes. It is to be noted that the refinement of the x-ray diffraction data of β-P_4S_3 using the molecular-form factor appropriate for the isotropically rotating molecules proved to be not satisfactory.[14] This may be because the molecules in the plastic phase are not rotating isotropically. The rigid translational modes must all be there because the center of gravity of the molecule is still ordered, but they are not seen. It is generally believed that the rigid translational modes may

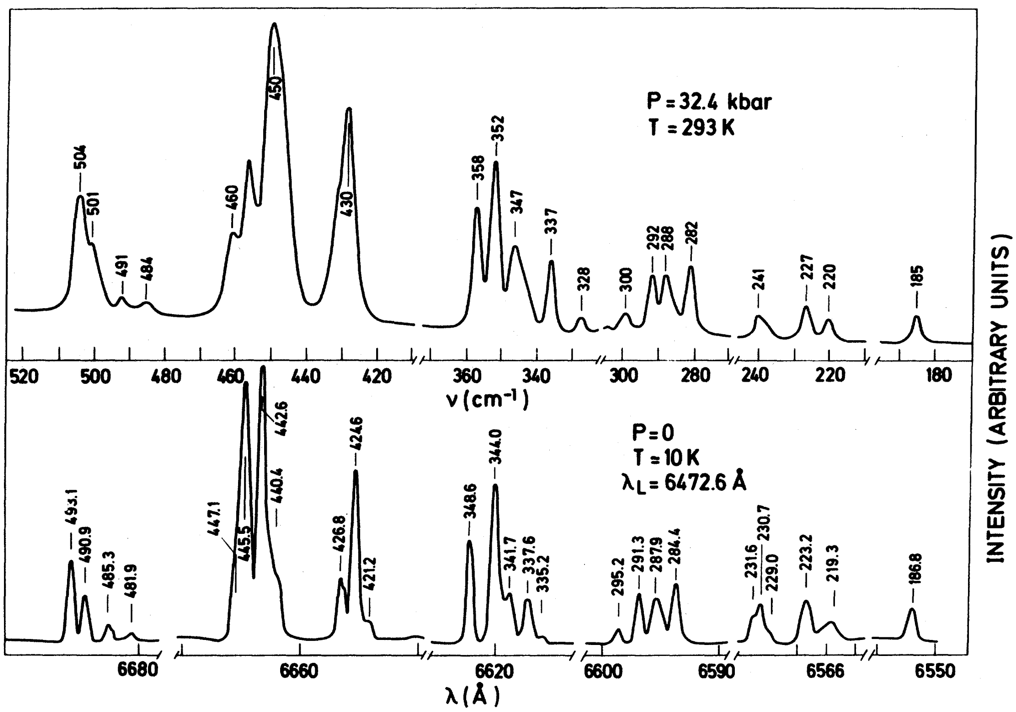

FIG. 10. Raman spectrum of α-P_4S_3 taken at ambient pressure and $T = 10$ K is shown along with the spectrum at $P = 32$ kbars and $T = 293$ K. The wave-number shifts are marked for the peaks. The qualitative correspondence between the two spectra is evident. The multiplicity is due to Davydov splitting (see text for explanation).

be far weaker and lie buried in the rather strong background scattering accompanying the Rayleigh scattered component, in the low-frequency region. The transition is reversible as seen by Raman spectroscopy and we did not observe such pronounced hysteresis effects as observed in specific-heat measurements.[12]

VII. VIBRATIONAL SCALING BEHAVIOR IN P_4S_3

The dimensionless quantity connecting the volume dilation $\Delta v/v$ with the fractional change in frequency is defined as the mode Grüneisen parameter γ_i,

$$\Delta\nu_i/\nu_i = -\gamma_i(\Delta v/v) = \gamma_i bP \;, \qquad (6)$$

where ν is the frequency, P is the pressure, and b is the compressibility. Zallen[1] first pointed out that the Grüneisen's approximation (all γ_i assumed to be equal) fails in the case of molecular crystals.[2] The Grüneisen's approximation predicts a set of points, all lying on or near a horizontal line in a plot of $\ln[1/\nu_i(d\nu_i/dP)]$ against $\ln\nu_i$. In the external mode region the points fall on the indicated horizontal line, while in the internal mode region $d(\ln\nu)/dP$ rapidly decreases. In this connection Zallen[1] has proposed a bond scaling relationship which connects bond stiffness with bond length, $k \sim r^{-6\gamma}$, where k is the force constant, r the bond length, and γ a bond scaling exponent of the order of unity, applicable to both intramolecular and intermolecular bonds. In the simplest model of a molecular crystal the bond-stiffness–bond-length scaling parameter γ is related to the external mode Grüneisen parameter γ_1 and the internal mode Grüneisen parameter γ_0 by the relation $\gamma_1 \sim 2\gamma$ and $\gamma_0 \sim (k_1/k_0)2\gamma$, where k_1/k_0 is the intermolecular to intramolecular force-constant ratio. The bond-stiffness–bond–length parameter γ and γ_1 differ only by a geometry-determined factor of the order of unity, while the internal mode Grüneisen parameter γ_0 is drastically reduced by the factor $k/k_0 \ll 1$. Qualitatively γ_1 is of the order of unity and is of normal size but γ_0 is reduced to values of the order of 10^{-2}. The abovementioned modification of the scaling law expresses the existence of disparate forces existing in a molecular crystal.[2]

VIII. SUMMARY AND CONCLUSIONS

The pressure and temperature dependence of the Raman spectrum of α-P_4S_3 has been investigated to elucidate the effect of decreasing volume on the phonon frequencies and to understand at the microscopic level the so-called crystalline-to-plastic

TABLE III. Comparison of Raman frequencies (cm^{-1}) at low temperature and high pressure.

		Phonon frequency $\nu(\mathrm{cm}^{-1})$			
Type	Assignment	$P=0$ kbar, $T=293$ K	$P=0$ kbar, $T\sim 10$ K	$P=32.4$ kbars, $T=293$ K	$P=86$ kbars, $T=293$ K
External modes		27.8	28.8	46	61
			33.8	50	
			36.4		
		36.2	39.8	56	69
			42.1		
			45.0	64	78
			50.2		
		46.0	54.7	76	93
				83	102
			63.0	93	113
				95	119
				97	128
					133
		58.5	67.7	102	138
					149
		72.0	81.9	122	153
					174
Internal modes	A_1	187	186.8	185	186
	E	220	219.3	220	223
			223.2	227	232
	E	227	229.0	241	248
			230.7		254
			231.6		
	E	288	284.4	282	278
					283
					287
			287.9	288	291
			291.3	292	293
					294
			295.2	300	307
	E	343	235.2	328	319
			237.6	337	332
					351
			341.7	347	355
			344.0	352	364
		347	348.6	358	369
	A_1	422	421.2	430	437
			424.6		
			426.8		
	A_1		440.4	450	458
		443	442.6		461
			444.5	456	475
			447.1	460	483
	A_1+E		481.9	484	497
		489	485.3	491	
			490.9	501	517
			493.1	504	524

phase transition near 314 K. Pressure has been particularly useful in revealing features unobservable under ordinary conditions. The following summarizes the findings of the present study.

(1) The intermolecular and intramolecular modes appear well separated in α-P_4S_3, a behavior typical of molecular crystals in which the intermolecular force constants are of the weak van der Waals type, while the intramolecular forces involve strong covalent bonding. The intermolecular

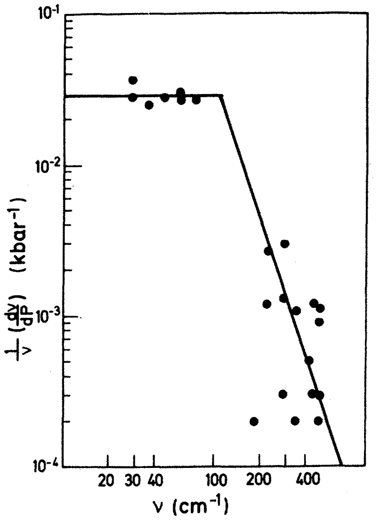

FIG. 11. Scaling law for Raman peaks in α-P_4S_3. The external modes fall in the horizontal line drawn, as would be expected, according to simple Grüneisen scaling behavior. The behavior of the internal mode frequencies is different. The plot reveals the disparities in the bonding that exists in the molecular α-P_4S_3 (see text for further explanation). The slope for the internal modes from $\gamma_i \sim \nu_i^{-2}$ and $\nu_i \sim K_i^2$ and $\gamma_i \sim K^{-1}$ is approximately obeyed.

or the external mode frequencies rapidly increase with pressure while the pressure dependence of the internal frequencies are found to be much smaller. Thus pressure differentiates the strength of the bonds.

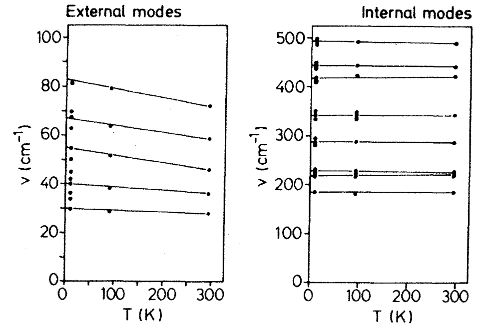

FIG. 12. Temperature dependencies of the Raman frequencies of α-P_4S_3. External and internal mode regions are separately exhibited. The internal mode frequencies vary very little with temperature.

(2) Pressure in general enhances intermolecular interactions. This results in increased spectral expansion and thereby reveals Davydov splitting of the internal mode frequencies which are not resolved under normal conditions, a fact found in earlier studies in other molecular crystals. The same end result can be achieved when the linewidths are drastically reduced by cooling down to low temperatures. The low-temperature spectrum and the high-pressure spectrum are thus remarkably similar in appearance.

(3) The Raman spectrum across the crystalline-to-plastic transition has revealed that the external mode spectrum of the α-P_4S_3 disappears in the high-temperature phase, leaving only a wing to the Rayleigh-scattered central component. The

TABLE IV. Relative sensitivity to pressure and temperature, and the separation of the explicit phonon contribution and the implicit volume-driven contribution to the temperature coefficient for phonon frequencies in crystalline α-P_4S_3. $a = 2.4 \times 10^{-4}$ K^{-1} and $b = 1.7 \times 10^{-2}$ kbar^{-1}, where a is the thermal expansion and b the compressibility. $\Theta = (\partial\nu/\partial T)_v/(\partial\nu/\partial T)$ (see Ref. 2).

Type	ν (cm^{-1})	$-\left(\frac{d\nu}{dT}\right)_P$ (cm^{-1}/K)	$\left(\frac{d\nu}{dP}\right)_T$ (cm^{-1}/kbar)	$\left(\frac{dT}{dP}\right)_\nu$ (K/kbar)	Θ	$\left(\frac{d\nu}{dT}\right)_v$ (cm^{-1}/K)
External modes	28	0.0067	0.785	117.1	−0.69	
	36	0.0133	0.908	68.2	0.02	
	46	0.0307	1.308	42.6	0.39	
	59	0.0300	1.669	55.6	0.20	
	72	0.0380	1.985	52.2	0.25	
Internal modes	187	0.0	0.0385			0.0006
	220	0.0	−0.0769			−0.0011
	227	0.0	0.6154			0.0089
	288	0.0	0.0769			0.0011
	343	0.0	−0.3077			−0.0044
	347	0.0	0.3846			0.0055
	422	0.0	0.2308			0.0033
	443	0.0	0.1538			0.0022
	488	0.0	0.4255			0.0061

spectrum of the high-temperature phase is found to be remarkably similar to the solution spectrum. From this it is concluded that the molecules have gained almost isotropic rotational freedom in the high-temperature phase; the external modes of the α phase are believed to be due to librational motion of the molecules in the unit cell. In the plastic phase, the center of gravity of the molecules occupy lattice sites, preserving long-range order, but the orientational ordering is lost. The lattice modes associated with the rigid translational ordering should still be present but they are not observable under present conditions. It is possible that these modes may be forbidden when a molecule is rotating, or they are so weak that they are hidden in the strong wing accompanying the central component.

(4) The pressure data have been used to test the applicability of the vibrational scaling law proposed by Zallen.[1] The results for α-P_4S_3 are in accordance with previous findings on As_4S_4, namely that $(1/\nu)(d\nu/dP)$ is very large and remains constant for the external modes but rapidly drops in the internal mode region, varying over two orders of magnitude. The behavior is believed to be due to the different type of bonding forces that can exist in a molecular crystal, viz., van der Waals force between molecules and covalent forces within the molecule.

(5) The temperature dependence of the phonon frequencies (Fig. 12) has been used to evaluate the volume-driven contribution ("implicit") to $(d\nu/dT)$ against the so-called "explicit" contribution arising from the effect of temperature on the vibrational amplitudes, when the volume of the crystal is held constant. The "implicit" contribution (see Table IV) dominates the external mode frequencies, which is consistent with similar findings on As_4S_4. Such evaluation was not possible for the internal modes of α-P_4S_3, because of the negligible effect of temperature on the internal frequencies. In conclusion it can be stated that α-P_4S_3 exhibits high-pressure behavior consistent with what has been proposed by Zallen and Slade[2] for a typical molecular system.

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