Free energy and the relative stability of the phases of solid tetracyanoethylene with pressure and temperature

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The concept of comparing the Gibbs free energy $G(P,T)$ for different phases is used to understand the phase diagram of an organic molecular solid for the first time. Calculations are carried out for tetracyanoethylene, since it exhibits rather unusual phase transitions with large hysteresis, and its two crystalline phases have almost equal static potential energy. The lattice part of the free energy has a contribution from the molecular packing and the phonon density of states, which are calculated using a six-exponential potential between nonbonded atoms. It is shown that the low-symmetry monoclinic phase is stabilized at high temperature due to its higher vibrational entropy, as compared to the cubic phase which is stabilized at high pressure due to its lower volume. The calculated phase diagram is in good qualitative agreement with experimental observations.

I. INTRODUCTION

Complex molecular solids are usually found to exhibit several polymorphic phase transitions. In particular, the first-order transitions, which involve large rearrangements of molecules and large hysteresis, are poorly understood. A study of the Gibbs free energy as a function of pressure and temperature is useful for understanding not only the relative stability of the phases, but also the important factors contributing to the stability. However, the above approach is not usually followed due to its inherent difficulties. While, for insulators, the electronic part of the free energy may be considered invariant, the part due to molecular packing and thermal vibrations itself requires a good knowledge of the interatomic potentials and extensive computations.

The organic solid, tetracyanoethylene (TCNE), shows very interesting and rather unusual phase-transition behavior.[1] At atmospheric pressure, the cubic phase I (space group $Im3$) transforms to the monoclinic phase II ($P2_1/n$) on heating at 318 K, and the transition is irreversible on cooling to 5 K. However, on application of a pressure of 2 GPa at 295 K, the reverse transition from phase II to I is observed via an intermediate metastable amorphous phase III. Recently, we carried out detailed studies of the thermal vibrations in TCNE by coherent inelastic neutron scattering,[2] Raman scattering,[3] and also by lattice dynamical calculations.[2-4] These calculations, which were based on the six-exponential atom-atom pair potential between nonbonded atoms and certain parameters to define the low-frequency internal vibrations, agreed very well with the experimental results.

We have now extended the calculations to obtain the vibrational spectrum (density of states) as a function of pressure in the two crystalline phases. Further, we have calculated the lattice part of the Gibbs free energy as a function of pressure and temperature, separately for the cubic and the monoclinic phases. Since the stable phase

is the one with the lower free energy, the equilibrium phase diagram is obtained. It is implicitly assumed that the phases are perfect, and so contributions from defects have been ignored. The agreement of the results of the calculation with those from the experiments is considered very satisfactory in view of the complexity of the structures that are considered and the simplicity of the potentials used. We believe that this work represents the first study of this type for any complex organic molecular solid. A closer comparison of the components of the free energy of the two phases has revealed that, although the cohesive energy in the two phases is nearly the same, the stability of the low-symmetry monoclinic phase at high temperature and low pressure is due to its higher vibrational entropy and higher volume, as compared to that of the cubic phase.

As mentioned above, an amorphous phase also occurs as an intermediate metastable state during the transition from the monoclinic to the cubic phase at high pressure. However, we have not evaluated the free energy in this phase since the structural data are not available. We are planning to study the amorphous phase using computer simulation.

In the following, first we shall summarize the model of the interatomic potential and the lattice dynamics,[2-4] and present results of this model on molecular packing and the vibrational spectrum at various pressures. Next we shall describe calculation of the free energy of the two crystalline phases as a function of pressure and temperature and discuss the phase transition. We shall also present results on the partial density of states corresponding to the various thermal vibrations in TCNE.

II. THEORETICAL MODEL

The molecule of TCNE has certain internal vibrations which occur at low frequencies and which are well separated from the remaining internal vibrations.[2,4] The intermolecular interactions in the solid state would manifest significantly only in the low-frequency internal vi-

brations and the external rigid-body vibrations of the molecules. The remaining internal vibrations would be essentially invariant during phase transitions. We have therefore adopted the "semirigid molecular model" of lattice dynamics[2,4] which involves only the low-frequency vibrations. For each TCNE molecule we need to consider the seven internal vibrations which occur below 10 THz (Refs. 2 and 3) and the six external vibrations, namely the three translations and three librations. This gives a total of 13 degrees of freedom per molecule. The monoclinic phase,[2] with two molecules in the primitive cell of the space group $P2_1/n$, has 26 modes for each wave vector. The cubic phase,[4] with three molecules in the rhombohedral primitive cell of the bcc space group of $Im3$, has 39 modes for each wave vector.

The intermolecular potential is obtained by summing the six-exponential potential for all pairs of nonbonded atoms belonging to different molecules. We used the parameters of the potential as given by Govers,[5] who obtained them by fitting to the equilibrium structures and cohesive energies of several molecular crystals. Contribution from the intramolecular potential is included only in the self-force-constants of the internal vibrations through certain adjustable parameters, which were obtained by using the known frequencies at ambient pressure. The intermolecular potential contributes to all the force constants.

The structure in a given phase, at a given pressure and zero temperature, can be obtained by minimizing the Gibbs free energy $G(P,T=0)=U+PV+E_0$ (U is the static potential energy, PV is the product of the pressure and the volume, and E_0 is the zero-point energy), with respect to the structural variables, namely, the lattice parameters, the positions, the orientations, and the internal configurations of the molecules; while keeping the space group symmetry unchanged[6] in the minimization process. However, the variation of E_0 can be ignored as compared to the variation of $U+PV$, for typical organic crystals like TCNE. In fact, for TCNE the vibrational pressure arising due to the zero-point energy is only about 0.1 GPa. It is also found[3] that the variation in the internal configuration of the TCNE molecule in a given phase is negligible for pressures up to 4 GPa. The equilibrium structure thus obtained at a given pressure is used in the quasiharmonic dynamical calculations.[3]

The model has been successfully used for the monoclinic phase at ambient pressure in the calculation of the phonon dispersion relation and the one-phonon cross sections for neutron scattering experiments.[2] Good agreement was obtained between the calculated and the measured dispersion relation and neutron intensities.[2] We have also calculated the phonon frequencies of zero wave vector at high pressures and found the results in fair agreement with Raman-scattering experiments, in both the monoclinic and cubic phases.[3] However, in these calculations in the monoclinic phase, one of the internal modes, namely the symmetric out-of-plane rocking mode, occurred at a much higher frequency than the experimental value.[2,3] To remedy this situation, we have now improved the parameters[2] of the intramolecular potential from the earlier values of 3.1, 7.5, and 10.6 THz to 3.1, 7.3, and 7.5 THz. The values for the cubic phase, of 3.9, 7.3, and 8.2 THz, are the same as in our earlier work.[3] The slight difference in these values, which were obtained for the two phases using the Raman frequencies at ambient pressure, may be attributed to the difference in the values of the bond angles[7,8] of the molecule in the two phases.

In order to obtain the phonon density of states, which is needed in the calculation of the free energy, we need to integrate over all the wave vectors in the irreducible Brillouin zone (IBZ). The techniques of analytical geometry may be used[9] to obtain the wave vectors belonging to the IBZ. However, for this purpose, we have developed a small computer program which is based on the following simple technique: The program is suitable for crystals of any space group. Instead of considering the conventional Brillouin zone (BZ) in the form of the Wigner-Seitz cell in the reciprocal space, we start with a primitive cell made of the reciprocal-lattice vectors. We then partition this cell with a certain mesh size along each of the reciprocal-lattice vectors, and collect the coordinates of all the mesh points (wave vectors). Next we obtain groups of points that are equivalent by symmetry, and retain only any one point from each group, with a weightage equal to the number of points in the group. We have thus obtained all the wave-vector points corresponding to the IBZ with their proper

TABLE I. The calculated results on the pressure (P) variation of the molecular volume V, static potential energy U, zero-point energy E_0 due to the thermal vibrations of the semirigid molecule, and the free energy $G(P,T)$ at temperature $T=0$ K; all normalized to one molecule of TCNE. Here $G(P,T=0)=U+PV+E_0$. 1 GPa nm^3 = 6241 meV.

		Cubic phase					Difference[a]		
P (GPa)	V (nm^3)	U (meV)	E_0 (meV)	G ($T=0$) (meV)	ΔV (nm^3)	$P\Delta V$ (meV)	ΔU (meV)	ΔE_0 (meV)	ΔG ($T=0$) (meV)
0	0.1361	−748.4	112.4	−636.0	0.0009	0	1.2	−7.5	−6.3
1.0	0.1251	−720.3	126.8	187.4	0.0013	8.2	5.0	−7.8	5.4
2.0	0.1187	−657.6	137.2	961.0	0.0013	16.6	4.4	−7.7	13.3
3.0	0.1140	−586.1	146.0	1694.4	0.0013	24.9	7.8	−7.8	24.9
4.0	0.1104	−509.0	153.5	2400.7	0.0013	32.1	14.0	−7.8	38.3

[a] This gives the values for the monoclinic phase minus that for the cubic phase. We estimate numerical errors of about 1 meV in these various values of energies, due to the minimization procedure in calculating the structure, and the particular sums of potentials over the atomic pairs, etc.

weights. We could choose that wave-vector point from each group of the equivalent points which is closest to the zone center, and then the set of points so obtained would be the same as those in the IBZ obtained from the Wigner-Seitz cell. However, this is not necessary to do.

For the monoclinic phase, we have used a $10 \times 10 \times 10$ mesh in the BZ. This resulted in 312 independent wave vectors in the IBZ, with their weights varying between 1 and 4. For the cubic phase, with a mesh size of $16 \times 16 \times 16$ in the BZ, we obtained 213 wave vectors in the IBZ with their weights between 1 and 48. Note that

the ratio of the volume of the IBZ to that of the BZ is $\frac{1}{4}$ in the monoclinic phase and $\frac{1}{48}$ in the cubic phase.

The phonon density of states is obtained by the histogram sampling of frequencies over bins of 0.1 THz and then smoothened by Gaussians of full width at half maximum (FWHM) of 0.2 THz. The results at various pressures are presented in Figs. 1 and 2 for the cubic and the monoclinic phases, respectively. With increasing pressure, the phonon spectra have shifted to higher frequencies, which is a result consistent with the earlier calculations[3] on the zero-wave-vector phonons. A more impor-
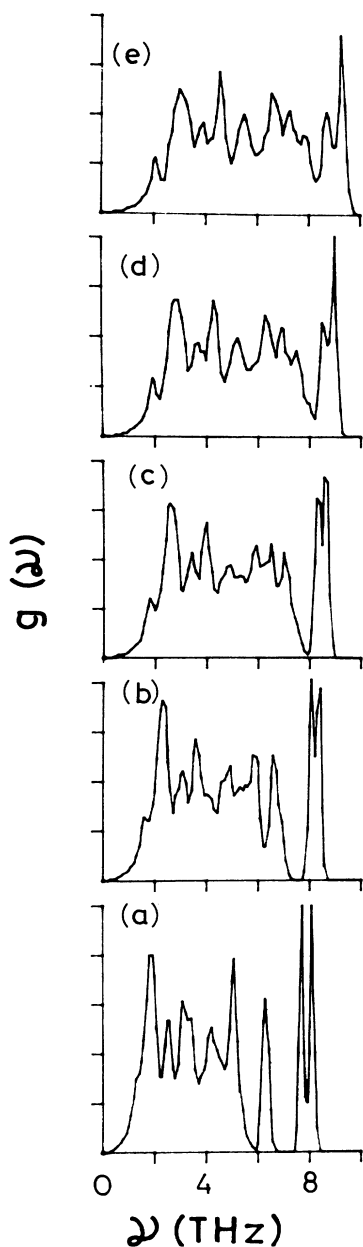

FIG. 1. The phonon density of states $g(\nu)$ (arbitrary units) for the cubic phase of TCNE, as calculated using the semirigid molecular model for pressures of (a) 0 GPa, (b) 1 GPa, (c) 2 GPa, (d) 3 GPa, and (e) 4 GPa.
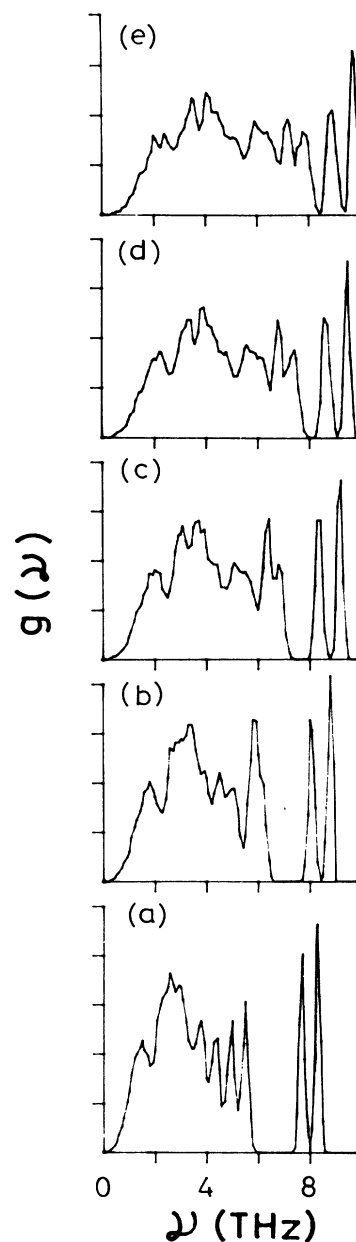
FIG. 2. Same as in Fig. 1 for the monoclinic phase of TCNE.

tant result is, however, the significant difference between the spectra for the two phases. The spectra for the monoclinic phase have a higher density of states at low frequencies compared to those for the cubic phase. Also the average frequency of the spectra for the monoclinic phase is somewhat lower. The implication of these features of the spectra on the free energy and the phase transition will be discussed later in the paper. Other results on the pressure variation of the molecular volume, static potential energy, and the zero-point energy, which are also required in the calculation of the free energy, are given in Table I.

III. FREE ENERGY

We need to evaluate the lattice part of the Gibbs free energy as a function of pressure P and temperature T. In the quasiharmonic approximation, the free energy has contributions from the static potential energy, pressure energy, vibrational energy, and vibrational entropy. The free energy is given by

$$G(P,T)=U(P)+PV(P)+ \int dv\, g(v,P)((hv/2)+kT \ln\{1-\exp[-hv/(kT)]\}) , \tag{1}$$

where $V(P)$ is the volume per molecule; $U(P)$ is the static potential energy per molecule, when all the atoms are located at their equilibrium positions; and $g(v,P)$ is the phonon density of states at frequency v, normalized for one molecule. Here we have ignored the relatively small temperature dependence of U, V, and g compared to their pressure dependence, since the variation in these quantities over the temperature range of 0 to 300 K is less than their variation due to a pressure change of a fraction of 1 GPa. Moreover, such variation with temperature is similar for the monoclinic and the cubic phases, and therefore would not significantly alter the relative stability of these phases on the P-T diagram.

Figures 3 and 4 illustrate the variation of the free energy with pressure and temperature, respectively, and show the relative stability of the two phases. In Fig. 5 we present the calculated phase diagram which indicates the relative stability of the cubic and the monoclinic phases on the P-T diagram. The figure clearly shows that while the monoclinic phase is stable at high temperature, the cubic phase is stable at high pressure. This is in agreement with the experimental observations.[1] How-

ever, the calculated transition pressure of 2.6 GPa at 295 K is somewhat higher than the experimental value of about 1 GPa (the value of 1 GPa is obtained by averaging over the hysteresis cycle of 0 to 2 GPa). This essentially indicates the deficiency of the six-exponential potential function, and will be discussed in the following. Moreover, the observed phase transition has a rather large hysteresis of about 2 GPa, which we believe is due to the large activation energy[1(b)] of 2.4 eV during the transition.

We recall that the potential, as used in the present calculation, was not derived particularly for TCNE, but was obtained by fitting over the characteristics of a number of similar molecular solids.[5] The pair potential is isotropic in character and does not allow for anisotropy of the interaction. Also it does not explicitly include Coulombic and many-body interactions. With such shortcomings of the potential, one may not expect good quantitative estimates of the differences between the two phases. However, with this in mind, we shall consider the various components of the free energy to understand their significance in the phase stability.
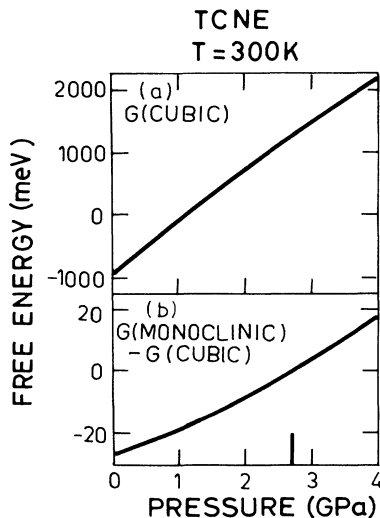

FIG. 3. Variation of the free energy $G(P,T)$ as a function of pressure for $T=300$ K (a) for the cubic phase of TCNE, (b) for the difference G(monoclinic) $-G$(cubic).
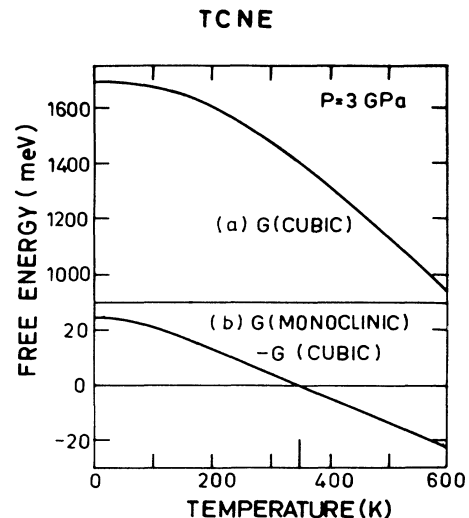

FIG. 4. Variations of the free energy $G(P,T)$ as a function of temperature for $P=3$ GPa; (a) for the cubic phase of TCNE, (b) for the difference G(monoclinic) $-G$(cubic).
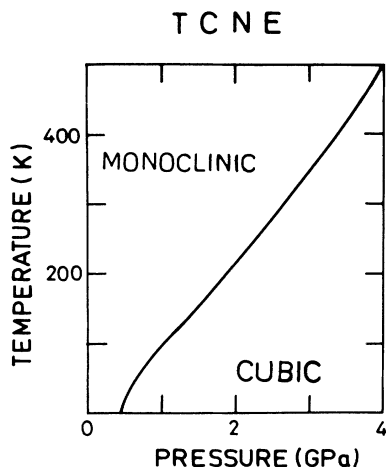
T C N E

FIG. 5. Relative stability of the monoclinic and the cubic phases of TCNE as obtained by comparing their free energies as a function of pressure and temperature.

From Table I we can make a comparison between the two phases of TCNE. At all the pressures for which calculations have been carried out, the calculated volume for the cubic phase is lower while the zero-point energy is higher. We also notice from Table I that, while there is a large variation in the values of V, U, and E_0, as a function of pressure, the difference between these values for the two phases varies much less rapidly. The differences between the volumes and the zero-point energies of the two phases are essentially invariant over the range of 0 to 4 GPa. In fact, the difference $\Delta G(P,T =0)$ varies with pressure largely due to the term $P\Delta V$. Here Δ symbolizes the difference of the monoclinic phase from the cubic phase.

Clearly the cubic phase is favored at high pressure (at low temperature) essentially due to its lower volume, and partly due to the lower static potential energy. However, at high temperature, the contributions from vibrational energy and vibrational entropy must be considered. As temperature increases, the vibrational energy E for each mode approaches kT for both phases and so the difference ΔE between the two phases becomes negligible. The difference in the vibrational entropy favors the monoclinic phase, which is therefore stable at high temperature. The phase transition is essentially obtained by the competition of the terms $P\Delta V$ and $T\Delta S$, although the transition pressures and temperatures are significantly influenced by ΔU and ΔE also. We may also note that since the variation of phonon frequencies as a function of pressure, as calculated, is similar in the two phases, the transition pressures and temperatures are only slightly influenced by such variation. For similar reasons we have ignored the variation of frequencies with temperature, both due to explicit anharmonicity and the thermal expansion.

We note that the calculated volume of the monoclinic phase is larger by about 1% than that of the cubic phase. However, the value obtained from experiments[8] is about 5%. Thus, although the sign of ΔV as calculat-

ed is in agreement with experiments, the magnitude of ΔV as calculated is much lower. This explains why the calculated value of the pressure of 2.6 GPa at the phase transition at 295 K is higher than the experimental value of about 1 GPa.

We wish to mention that often one seeks to understand the relative stability of phases by only comparing their static potential energies. We find that for TCNE, at zero pressure and temperature, the difference between the potential energies of the two phases is more than compensated by that between their zero-point energies. So it is important to also consider the vibrational terms in the free energy, particularly when the potential energy difference is small.

Now we shall discuss how the details of the phonon-frequency spectrum may influence the free energy. At a given pressure and temperature, the contribution to the free energy from a phonon of frequency v is given by

$$G = (hv/2) + kT \ln\{1 - \exp[-hv/(kT)]\} . \tag{2}$$

The change ΔG in this contribution, only due to an infinitesimal shift Δv in the frequency v, is

$$\Delta G = \Delta v (n + \tfrac{1}{2}) h , \tag{3}$$

where

$$n = 1/\{\exp[hv/(kT)] - 1\}$$

is the population of the phonon. The limiting values of $\Delta G/\Delta v$ are $h/2$ and kT/v, for $kT \ll hv$ and $kT \gtrsim hv$, respectively. Since $(n + \tfrac{1}{2})h$ is always positive, the free energy will shift in the same direction as the frequency, and the shift in the free energy per unit shift in frequency will be larger at higher temperature.

It is also clear from the above that $\Delta G/\Delta v$ is larger for smaller v. In particular, $\Delta G/\Delta v \approx kT/v$ for $hv \lesssim kT$ or $v \lesssim 6$ THz at 295 K. Therefore, at a given temperature, any shift of the low-frequency phonons will be more effective in changing the free energy than a similar shift of the higher-frequency phonons; although the total free energy will have contributions from all the phonons. By comparing the frequency spectra of the monoclinic and cubic TCNE, as given in Figs. 1 and 2, we find that the spectra for the monoclinic phase, in the low-frequency region of below 2 THz, are shifted to lower frequencies as compared with the spectra of the cubic phase in the same region. This shift may result in lower free energy due to these phonons, and thus favor the stability of the monoclinic phase at high temperature.

IV. PARTIAL DENSITY OF STATES

We also calculated the partial density of states $g^i(v)$, corresponding to vibrations of individual coordinates or degrees of freedom $(i = 1,2, \ldots, 13)$, namely, the three translations and three librations of the molecules separately about the three principal axes of inertia of the molecule, and each of the seven internal vibrations of the semirigid TCNE molecule.[2] Suppose $\xi(\mathbf{q}_p j)$ represents the normalized root-mass-weighted eigenvector of the jth phonon (belonging to the jth branch in the disper-
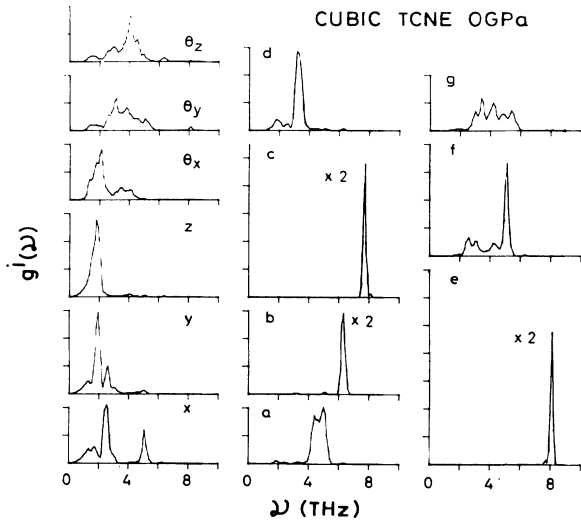
FIG. 6. The partial phonon density of states $g^i(v)$ (arbitrary units) for the cubic phase of TCNE at $P=0$ GPa. $i=1,\ldots,13$ correspond, respectively, to the translations about the X, Y, and Z principal axes of inertia of the molecule (Refs. 2 and 4), librations about these X, Y, and Z axes, and the seven internal vibrations (Ref. 2), namely, $a=$scissoring (S,ip), $b=$scissoring (A,ip), $c=$rocking (S,ip), $d=$rocking (A,ip), $e=$rocking (S,op), $f=$rocking (A,op), $g=$twisting (op); where S represents symmetric, and A represents antisymmetric, about the center of inversion, ip is in the plane, and op is out of the plane of the molecule. The principal X axis is perpendicular to the plane of the molecule, while the principal Y and Z axes lie in the plane (Refs. 2 and 4).

sion relation) of wave vector $\mathbf{q}_p$ and frequency $v(\mathbf{q}_p j)$, and has components $\xi_i(k,\mathbf{q}_p j)$ corresponding to the vibrational amplitude along the ith coordinate of the kth molecule. Then the contribution of a phonon of frequency v to the partial density of states $g^i(v)$ will be proportional to
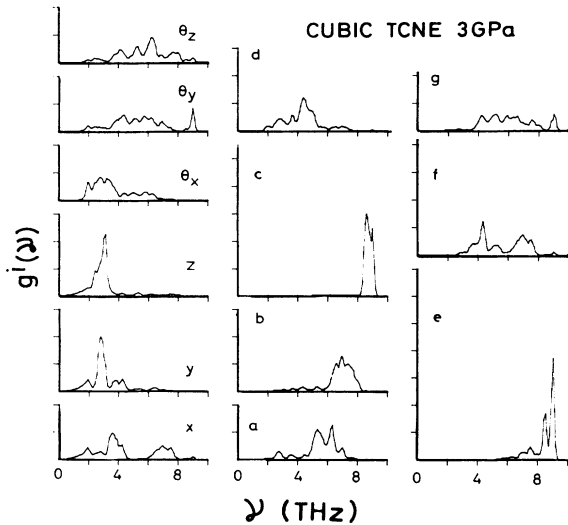
$$\sum_k |\xi_i(k,\mathbf{q}_p j)|^2 .$$

Thus we have

$$g^i(v)=A\sum_{p,j} d\mathbf{q}_p\delta[v-v(\mathbf{q}_p j)]\sum_k |\xi_i(k,\mathbf{q}_p j)|^2 , \qquad (4)$$

where

$$A=\left[N\sum_p d\mathbf{q}_p\right]^{-1} ,$$

$d\mathbf{q}_p$ is the weight associated with the wave vector $\mathbf{q}_p$ of

FIG. 8. Same as in Fig. 6, for the monoclinic phase of TCNE at $P=0$ GPa.

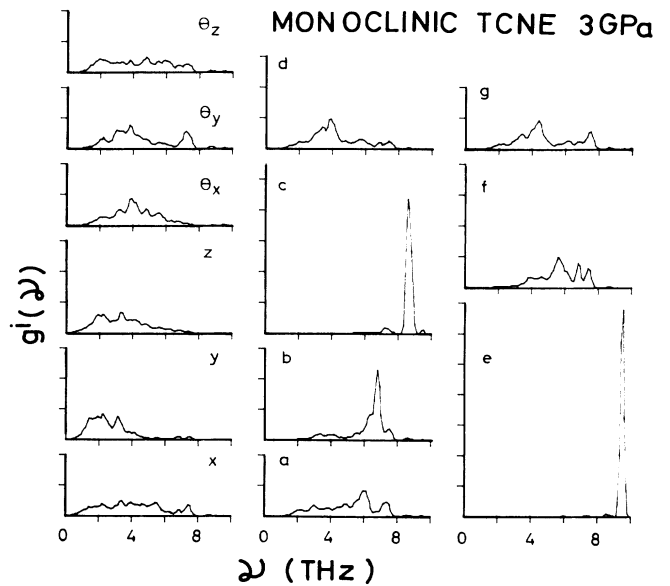FIG. 7. Same as in Fig. 6, for the cubic phase of TCNE at $P=3$ GPa.

FIG. 9. Same as in Fig. 6, for the monoclinic phase of TCNE at $P=3$ GPa.

the pth mesh point in the Brillouin zone, and the sum k extends over the N molecules in the unit cell, $i = 1, \ldots, 13$ and $j = 1, \ldots, 13N$. The $g^i(v)$ is normalized to vibrations of one molecule. Clearly the total density of states is just the sum of all the partial densities,

$$g(v) = \sum_i g^i(v) = A \sum_{p,j} d\mathbf{q}_p \delta[v - v(\mathbf{q}_p j)] \; ,$$

as   (5)

$$\sum_{i,k} |\xi_i(k,\mathbf{q}_p j)|^2 = 1; \quad \text{and also} \quad \int g(v)dv = 13 \; .$$

The results on the partial density of states are given in Figs. 6–9 for the cubic and the monoclinic phases at pressure 0 and 3 GPa. These results are rather interesting and useful. It is now possible to observe the behavior of each vibration in terms of its frequency distribution and coupling with other vibrations. Significant differences are visible between the distributions of the translational and rotational motions, and also between the distributions of these motions about the different principal axes of inertia of the molecule. In particular, differences are observed between the distributions of the vibrations that occur in the plane and those out of the plane of the molecule.

When the frequency distributions $g^i(v)$ for a set of vibrational coordinates ($i = i_1, i_2,$ etc.) overlap, the phonons of the overlapping frequencies would most likely involve coupled vibrations of these coordinates. In particular, when the frequency distribution of a certain internal coordinate is overlapping with the frequency distribution of the external coordinates, the phonons of the frequencies in the overlapping region would involve coupled vibrations of both the internal and the external coordinates, and therefore such phonon modes would not be purely external or internal modes, but would have mixed character. Further, one can study each vibration as a function of pressure, as well as compare its spectrum between the two phases. Such a study would give the average behavior of all the modes in the Brillouin zone, and would not be restricted to only certain modes.

As one might expect, with increase of pressure, the distributions broaden and shift to higher frequencies. These effects are more pronounced for the external vibrations than for the internal vibrations. Due to the faster shift for the external vibrations with pressure, new overlaps and couplings develop between the external and the higher-frequency internal vibrations.

These partial densities of states are also useful in evaluating the density of states, $g^{(n)}(v)$, as weighted with the neutron-scattering lengths, which can be compared with measurements by inelastic neutron scattering. We have obtained $g^{(n)}(v)$ by summing over the partial densities of the different coordinates, each weighted by a suitable factor containing the neutron-scattering lengths. We shall, however, not discuss the determination of $g^{(n)}(v)$ here.

V. SUMMARY

In this paper we have presented exhaustive calculations of the vibrational density of states, and its partial components for each degree of freedom, for the cubic and monoclinic phases of TCNE as a function of pressure. These results, along with those on the static potential energy and the volume in the two phases as a function of pressure, are used to evaluate the Gibbs free energy in the (P,T) space. By comparing the variation of the free energy, which is calculated separately for the two phases, we have derived the relative stability of the phases in the (P,T) space. The results are in good qualitative agreement with the experimental observations. We have further analyzed the variation in the various components of free energy, namely, the potential energy, volume, vibrational energy, and vibrational entropy. We have also discussed the influence of the details of the frequency distribution on the free energy and evaluated their importance in the relative stability of the two phases in TCNE.

[1](a) S. L. Chaplot and R. Mukhopadhyay, Phys. Rev. B **33**, 5099 (1986); S. L. Chaplot, Phys. Status Solidi A **92**, K23 (1985); (b) R. Mukhopadhyay, S. L. Chaplot, and K. R. Rao, Phys. Status Solidi A **92**, 467 (1985).

[2]S. L. Chaplot, A. Mierzejewski, G. S. Pawley, J. Lefebvre, and T. Luty, J. Phys. C **16**, 625 (1983).

[3]S. L. Chaplot, A. Mierzejewski, and G. S. Pawley, Mol. Phys. **56**, 115 (1985).

[4]S. L. Chaplot, J. Phys. C **18**, 2055 (1985).

[5]H. A. J. Govers, Acta Crystallogr. Sect. A **31**, 380 (1975).

[6]G. S. Pawley and K. Mika, Phys. Status Solidi B **66**, 679 (1974).

[7]S. L. Chaplot, A. Mierzejewski, and G. S. Pawley, Acta Crystallogr. Sect. C **40**, 663 (1984).

[8]D. A. Bekoe and K. N. Trueblood, Z. Kristallogr. **113**, 1 (1960); R. G. Little, D. Paulter, and P. Coppens, Acta Crystallogr. Sect. B **27**, 1493 (1971).

[9]V. K. Jindal and J. Kalus, J. Phys. C **16**, 3061 (1983).