Lattice dynamics, thermodynamic functions, and phase transitions of *p*-dichloro- and 1,2,4,5-tetrachlorobenzene

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The thermodynamic properties and phase transitions of p-$C_6H_4Cl_2$ and 1,2,4,5-$C_6H_2Cl_4$ have been studied, using an intermolecular potential function of the atom–atom type. The Debye–Einstein approximation to the density of states is checked against the complete calculation for the case of p-$C_6H_4Cl_2$. This approximation is sufficiently accurate for the calculation of thermodynamic properties. The behavior of the free energy in the vicinity of the phase transition is studied for both crystals. The calculations are consistent with experimental data.

INTRODUCTION

Semiempirical potentials for intermolecular forces in molecular crystals are usually obtained by taking into account a certain number of static and dynamic properties of a set of crystals; they are most useful if they can be related consistently with other physicochemical properties of these and other related crystals. An intermolecular force field for a series of chlorinated benzene crystals has been developed in this laboratory, based on the assumption of an intermolecular potential function of the atom–atom type in the Buckingham form. The parameters were refined adjusting observed heats of sublimation, crystal structures, and optical lattice vibration frequencies of C_6Cl_6, sym-$C_6H_3Cl_3$, and p-$C_6H_4Cl_2$ in its α and β phases.[1,2] Later on the transferability of the model was checked calculating the lattice frequencies of β-1, 2, 4, 5-$C_6H_2Cl_4$,[3] which showed good agreement with experiment. The crystal structure of α-1, 2, 4, 5-$C_6H_2Cl_4$ was determined from packing calculations, and with that structure the calculated lattice frequencies reproduce well the experimental values.[4] Table I shows the observed and calculated lattice frequencies of C_6Cl_6, 1, 3, 5-$C_6H_3Cl_3$, α- and β-p-$C_6H_4Cl_2$, and α- and β-1, 2, 4, 5-$C_6H_2Cl_4$, some of which have not been published previously; it is seen that the overall agreement is good. The molecules forming these crystals are nonpolar; the model does not seem to work too well for a polar molecule like 1, 2, 3-$C_6H_3Cl_3$.[5]

There are a number of crystal properties other than optically active frequencies and crystal structures which can be calculated once the intermolecular potential is known, particularly the frequency distribution throughout the Brillouin Zone, from which the thermodynamic properties can be obtained. In those cases where a phase transition exists the model should account at least qualitatively for it.

Some calculations of thermodynamic properties of molecular crystals have been performed, checking the self-consistency of several atom–atom potential models; in particular, structural and dynamical properties of crystalline N_2 have been calculated near the transition point.[6,7] For more complex crystals calculations are limited mainly to hydrocarbons, for which the existing potential parameters give consistent results for a large number of their physcochemical properties[8–10]; more recently these calculations have been applied to some fluorinated hydrocarbons,[11] although in this case no phase transitions have been studied.

In the present work we study the thermodynamic properties and phase transitions of p-$C_6H_4Cl_2$ and 1, 2, 4, 5-$C_6H_2Cl_4$ using the model mentioned above. It must be stressed that we cannot predict a phase transition, since we need to know the crystal structures of both phases for the calculation, nor go into the mechanism of the transition itself. However, we can calculate differential properties, gain information on the behavior of either phase, and check the consistency of the model.

CALCULATION OF THERMODYNAMIC FUNCTIONS

In the cases we are interested in there is a negligible distortion of the molecule upon crystallization. Therefore, the contribution of the intramolecular static energy to the thermodynamic functions is constant, and will be taken as the reference energy. This choice makes the calculated internal energy positive, since the zero point energy of the internal and external modes is large. Furthermore, the PV term in the Gibbs free energy is very small (< 5 cal/mole) and the Helmholtz free energy is used in the computations.

For a crystal with M molecules per unit cell and N atoms per molecule the free energy A per unit cell at temperature T is given by

$$A(T) = \Phi_{st} + \tfrac{1}{2} h \sum_\alpha \int_0^\infty \nu g_\alpha(\nu) d\nu + kT \sum_\alpha \int_0^\infty g_\alpha(\nu) \times \ln\left[1 - \exp\left(-\frac{h\nu}{kT}\right)\right], \quad (1)$$

where Φ_{st} is the static crystal energy, α ranges over the $3MN$ internal and external phonon branches, and $g_\alpha(\nu)$ is the corresponding vibrational density of states normalized by

$$\int_0^\infty g_\alpha(\nu)\, d\nu = 1 . \quad (2)$$

The second and third terms in Eq. (1) represent the zero point energy and the thermal crystal energy, respective-

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TABLE I. Observed and calculated optical lattice frequencies of C_6Cl_6, 1, 3, 5-$C_6H_3Cl_3$, *p*-$C_6H_4Cl_2$, and 1, 2, 4, 5-$C_6H_2Cl_4$.

Crystal	Symmetry	ν_{obs} (cm^{-1})	ν_{calc} (cm^{-1})
C_6Cl_6[a]	A_g	56	52
		45	40
		21	28
	B_g	54	51
		38	38
		25	26
	A_u	51	57
		...	40
	B_u	...	22
1, 3, 5-$C_6H_3Cl_3$[b]		57	54
		...	45
	A_1	46	44
		34	34
		30	29
		23	20
	B_1	61	59
		54	47
		46	45
		34	34
		...	30
	B_2	56	55
		44	43
		...	37
		32	33
		22	22
	B_3	58	55
		...	51
		48	45
		36	41
		31	31
α-*p*-$C_6H_4Cl_2$[c]	A_g	94	102
		53	48
		...	45
	B_g	103	105
		47	50
		27	28
	A_u	56	46
		38	32
	B_u	26	25
β-*p*-$C_6H_4Cl_2$[d]		84	77
		56	54
		45	42
α-1, 2, 4, 5-$C_6H_2Cl_4$[e]	g	...	88
		68	68
		55	62
		48	46
		43	38
		33	33
	u	...	90
		...	63
		...	47
β-1, 2, 4, 5-$C_6H_2Cl_4$[f]		58	61
	A_g	46	54
		35	35
	B_g	...	69
		49	48
		21	19
	B_u	...	71
		...	29
	A_u	...	64

[a]Calculated g modes, Ref. 23. Observed frequency at 300 K, Ref. 24.
[b]Calculated frequency, Ref. 23. Observed frequency at 300 K, Ref. 25.
[c]Calculated g modes, Ref. 23. Observed frequency at 300 K, Refs. 26 and 27.
[d]Calculated and observed frequency, Ref. 23.
[e]Calculated and observed g modes, Ref. 4.
[f]Calculated and observed g modes Ref. 4.

ly. The expressions for the internal energy $E(T)$, the entropy $S(T)$, and the specific heat $C_v(T)$ are easily deduced from Eq. (1).

In our case Φ_{st} is directly the packing energy, which with the atom–atom model is calculated as

$$\Phi_{st} = E_{pack} = \frac{1}{2}\sum_{ij} V_{ij}(r_{ij}) , \tag{3}$$

where the sum is extended over all atoms i, j belonging to different molecules. We have used atom–atom functions of the Buckingham form

$$V_{ij}(r_{ij}) = -Ar_{ij}^{-6} + B\exp(-Cr_{ij}) . \tag{4}$$

The values of the parameters A, B, and C for each type of interaction, involving C, H, and Cl atoms, are shown in Table II.

Once the inter- and intramolecular force fields are established it is possible to calculate the crystal frequencies throughout the Brillouin zone, and therefore the density of states. The calculation method used here is

TABLE II. Potential parameters for the atom–atom interactions involving C, H, and Cl atoms.[a]

Interaction	A (kcal Å^6)	B (kcal)	C (Å^{-1})
H–H	27.3	2654	3.740
H–C	125	8766	3.670
C–C	568	83630	3.600
C–Cl	−631	44200	3.653
H–Cl	1005	33300	3.623
Cl–Cl	3650	263000	3.510

[a]References 1 and 2.

given in detail in Refs. 12 and 13. We have found that for the crystals under study there is a negligible coupling between internal and external modes, and therefore the rigid body approximation has been used; since the very small dispersion of the internal modes is also neglected, a specification of the intramolecular force field is unnecessary if all the fundamental vibration frequencies are known.

The density of states for the lattice modes was calculated by dividing the irreducible part of a reciprocal cell into a number of parallelepipeds of identical shape, solving the secular equation at points k in their center, getting ν_k and $\nabla_k \nu_k$, and extrapolating the frequencies linearly throughout the parallelepiped according to a method proposed by Raubenheimer and Gilat[14,15] and adapted to molecular crystals by Bonadeo and Taddei.[13] In order to simplify the calculation the sampling zone was chosen as a rectangular prism which contained nonequivalent parts of several Brillouin zones. Care was taken as to avoid the Brillouin zone boundaries in the choice of the point mesh.

Although these calculations are not too difficult to perform, they present another problem: they are very lengthy, and therefore extremely costly in terms of computer time. This leads to the search for alternative simpler models, which must be contrasted with the more exact calculation in order to evaluate their degree of accuracy. One approach, which has been used with success for the simpler crystals of α- and γ-N_2,[6] consists in solving the secular equation for $\mathbf{k}=0$, and adopting the Einstein approximation for the $6M-3$ optical branches and the Debye model for acoustic modes, taking as the Debye cutoff frequency that of the lowest lying optical mode. Since the internal modes are also treated in the Einstein approximation, the vibrational contribution to the free energy per unit cell can be written as

$$A_{\mathrm{vib}}(T) = \sum_{i=1}^{3MN-3} \tfrac{1}{2} h\nu_i(\mathbf{k}=0) + kT \ln\{1-\exp[-h\nu_i(\mathbf{k}=0)/kT]\} + \tfrac{9}{8} h\nu_D - kTD(h\nu_D/kT) , \quad (5)$$

where $\nu_i(\mathbf{k}=0)$ are the optical frequencies, ν_D is the Debye frequency, and $D(h\nu_D/kT)$ is the Debye function defined as

$$D(x) = 3/x^3 \int_0^x \frac{t^3}{e^t - 1} dt . \quad (6)$$

It must be noted that In Eqs. (1) and (5), $A(T)$ depends on the temperature both explicitly and via the packing energy and crystal frequencies, which for the lattice modes change appreciably over relatively large temperature ranges. However, in order to recalculate $g(\nu)$ and E_{pack} at various temperatures it would be necessary to know the crystal structure at these temperatures, which is not our case, and anyhow the calculation would become extremely cumbersome. Therefore, it was assumed that in the vicinity of the temperatures at which the structures were obtained the main contribution to the temperature effects is the statistical one, a fact that was verified by changing the values of $\nu(\mathbf{k}=0)$ in the Debye–Einstein approximation over ranges of experimental variation.

p-DICHLOROBENZENE

Crystalline *p*-dichlorobenzene has three known phases: γ, stable below 273 K; α, between 273 and 303 K; and β, stable between 303 K and the melting point at 326 K. Each of the three phases may be found by adequately varying the cooling conditions, at any temperature below 200 K, and the crystal may be almost indefinitely metastable.[16] The β phase is triclinic, space group $P\bar{1}$, with one molecule per unit cell[17]; the α and γ phases are monoclinic, space group $P2_1/a$, with two molecules in the unit cell.[18,19]

In the present work we are interested in the α–β transition. The optical frequencies for these phases have been calculated and show good agreement with experiment (see Table I). Furthermore, the dispersion curves of the β phase in the $(\xi, 0, 0)$ and $(0, \eta, 0)$ directions were obtained by inelastic coherent neutron diffraction by Reynolds *et al.*[20] for the completely deuterated crystal, and the calculations using the parameters of Table II compare well with the neutron data.[1] We have also calculated dispersion curves in several other directions of reciprocal space for both phases, and these are available upon request.

The lattice vibration densities of states for the α and β phases were calculated on the basis of the crystal structures determined at 295 and 300 K, respectively, according to the method outlined in the previous section. The calculation was performed on 500 and 2000 points in reciprocal space for the α and β phases, respectively, in order to obtain similar point densities for both phases. The contributions were channeled into intervals of 0.5 cm^{-1}, a choice which gives more than sufficient detail; it has been shown that for benzene[13] the linear extrapolation method is accurate to 0.1 cm^{-1}. The results are shown in Figs. 1 and 2, together with the densities of states in the Debye–Einstein approximation. It is clear that this approximation will be expected to be accurate *a priori* if the frequencies at the critical point Γ dominate the density of states; this could have been the case for both phases of p-$C_6H_4Cl_2$, since they do not have any other symmetry required regular critical point. Figure 1 shows that there is a fair correlation for the α phase, although the Debye model overestimates the low frequency part of the density of states; for the β phase (Fig. 2) $g(\nu)$ is rather flat, in contrast with the infinitely sharp Einstein model.

The complete densities of states were used to calculate, in the rigid body approximation, the contribution of the lattice vibrations to the internal energy, free energy, entropy, and specific heat in a range of temperatures near the phase transition. The results have been added to the internal mode and static contributions. Table III shows the values of the thermodynamic functions calculated for both crystal phases, together with sublimation energies and entropies, and available experimental data. The sublimation energy per molecule is calculated as

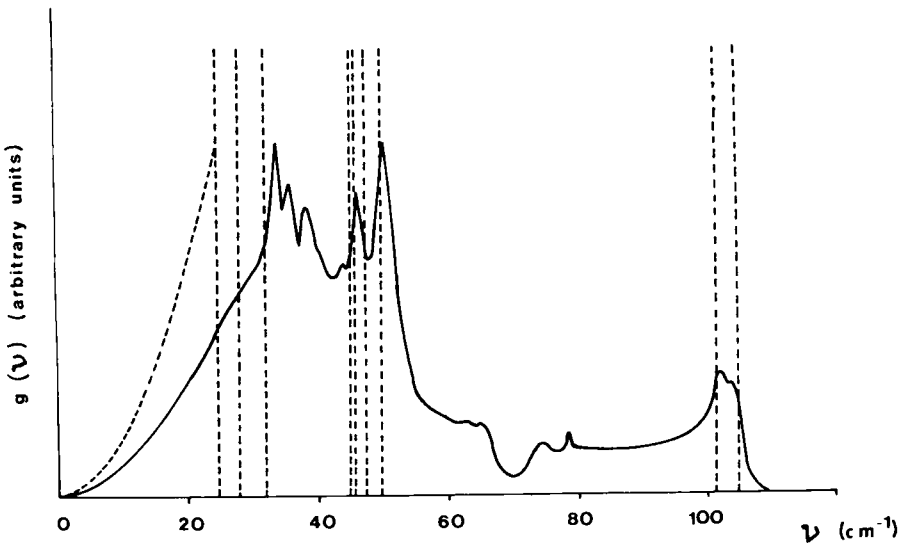

FIG. 1. Calculated density of states for α-p-$C_6H_4Cl_2$. ---- Debye–Einstein approximation.

$$\Delta H_{sub} = E_{gas} - E_{pack} - E_{lat} + \Delta E_{int} + PV\,, \tag{7}$$

where E_{gas} is the translational and rotational energy of the molecule in the gaseous phase ($3RT$), E_{pack} is the crystal packing energy, E_{lat} the contribution of the lattice frequencies to the internal crystal energy, and ΔE_{int} the difference between the internal vibrational energies in the gaseous and solid state; this difference is about -0.3 kcal/mole, i. e., less than 3% of the total heat of sublimation in our case; however, it could become important in less rigid molecules, where the crystal forces introduce appreciable molecular distortions.

It can be seen that the difference between the heats of sublimation of the two phases is small (< 1 kcal/mole), and of the order of the observed one. The values of the heats of sublimation are appreciably lower than the observed ones; this fact is readily explained since the potential parameters on which the calculation was based were originally adjusted to give packing energies which were equated to heats of sublimation, i. e., neglecting entropic effects. It is important to point out that this widely used approximation turns out to be, at least in our case, quite poor, since the entropic contribution is about 15% of the total heat of sublimation. The difficulty remains, however, that the density of states calculation is extremely lengthy, and not related in a direct way to the potential parameters, and it would be impossible to include such complication in a potential parameter refinement.

The sublimation entropy is calculated as $\Delta S_{sub} = S_{gas} - S_{cryst}$; the values obtained compare well with experiment. However, they are about 10% higher than those calculated from $\Delta S_{sub} = \Delta H_{sub}/T$, due to the fact that the calculated change in the Gibbs free energy in the crystal–gas transition is not strictly zero due to the approximations in the potential parameters discussed above.

Figure 3 shows the free energy vs. temperature plots for both crystal phases. It can be seen that both curves are almost coincident in the range 200–400 K; since

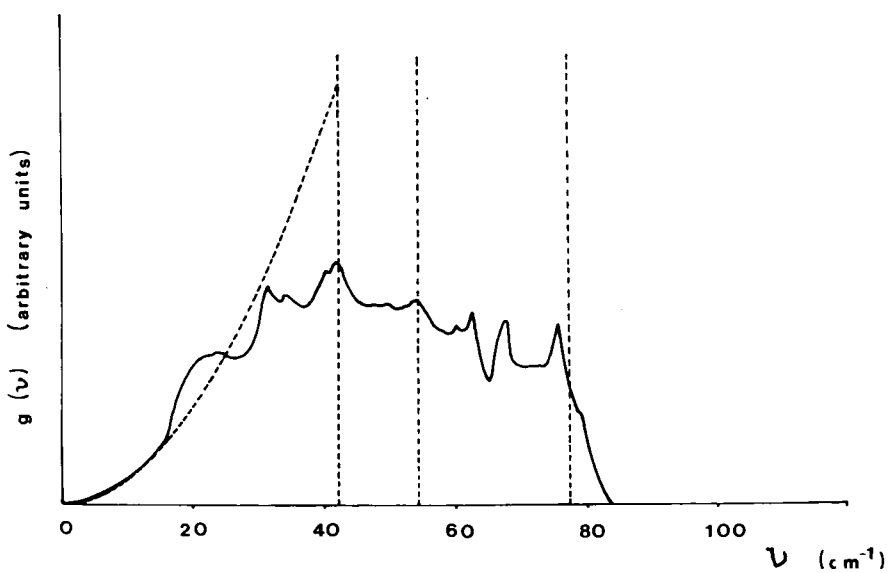

FIG. 2. Calculated density of states for β-p-$C_6H_4Cl_2$. ---- Debye–Einstein approximation.

TABLE III. Thermodynamic functions of α- and β-p-$C_6H_4Cl_2$. E_{pack} is the packing energy; E_{lat} and E_{int} are contributions from the lattice and internal modes to the internal crystal energy respectively; $E = E_{lat} + E_{int} + E_{pack}$; A_{lat} and A_{int} are contributions from the lattice and internal modes to the free energy; $A = A_{lat} + A_{int} + E_{pack}$; ΔH_{sub} is the heat of sublimation; S_{lat} and S_{int} are contributions from the lattice and internal modes to the crystal entropy; and ΔS_{sub} the sublimation entropy.

		Calculated		Experimental	
		Phase		Phase	
		α	β	α	β
Function	Units	300 K	318 K	300 K	318 K
E_{pack}		−15.13	−15.10		
E_{lat}		3.60	3.83		
E_{int}		52.26	52.76		
E		40.73	41.49		
	kcal/mol				
A_{lat}		−5.68	−6.30		
A_{int}		48.46	48.23		
A		27.65	26.83		
ΔH_{sub}		13.62	13.49	15.48±0.1	15.06±0.1[a]
S_{lat}		30.93	31.69		
S_{int}		12.68	14.24		
S		43.61	45.91		
ΔS_{sub}	cal/mole K	48.67	47.23	51.6±0.3	47.3±0.3[b]
$C_{v,lat}$		11.86	11.88		
$C_{v,int}$		17.50	18.70		
C_v		29.36	30.58		

[a]Reference 21.
[b]Calculated from data in Ref. 21, as $\Delta S_{sub} = \Delta H_{sub}/T$.

they do not show any difference in slope, no phase transition would be expected to exist. This apparent contradiction, however, is explained by the fact, mentioned before, that both phases exist in metastable form in the temperature range where the other one is stable—in fact, the β phase can be undercooled to liquid nitrogen temperature and maintained without changes almost indefinitely. This, of course, means that the difference in free energy must be extremely small over the whole temperature range considered, and due to the approximations involved it is not apparent in our calculation.

At this point we wish to focus our attention again on the Debye–Einstein approximation. It was stated before that, if accurate enough, it could be an undoubtedly advantageous procedure for calculating the lattice mode contributions to the thermodynamic functions. In order to check the model we have recalculated these functions for the α and β phases of p-$C_6H_4Cl_2$. The optical frequencies used were those calculated with our potential parameters, in order to preserve the internal consistency (see Fig. 2). The results obtained by using the approximation differ from those obtained with the complete density of states by less than 3% of the lattice mode contribution to the thermodynamic functions; in particular, the free energy curves are only slightly shifted, and neither their slopes nor their relative values are appreciably changed. These results are quite remarkable, given the simplicity of the model and the enormous computational simplification achieved by it. It is worthwhile to point out that since the optical fre-

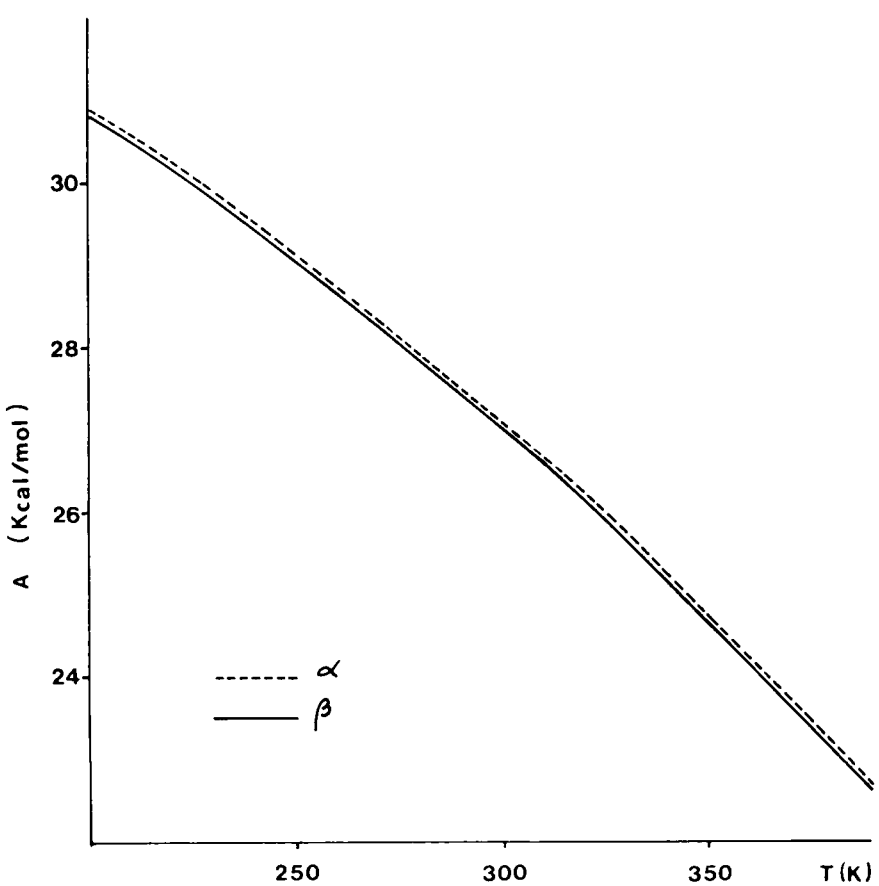

FIG. 3. Free energy vs temperature curves for α- and β-p-$C_6H_4Cl_2$.

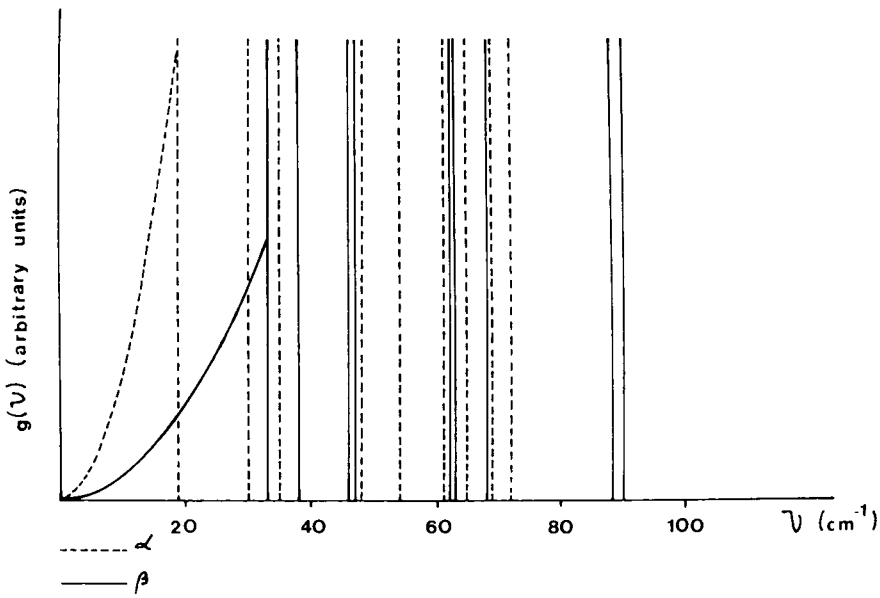

FIG. 4. Densities of states for α- and β-1, 2, 4, 5-$C_6H_2Cl_4$ in the Debye–Einstein approximation.

quencies and the Debye function have a relatively simple connection with the potential parameters, it is in principle possible to include thermodynamic properties via the Debye–Einstein density of states in a potential parameter refinement, and to overcome the difficulties mentioned before.

1, 2, 4, 5-TETRACHLOROBENZENE

There are two known phases of crystalline 1, 2, 4, 5-$C_6H_2Cl_4$: α, stable below 188 K, and β, stable between 188 K and the melting point. The crystal structure of the β phase has been completely solved by x-ray spectroscopy, and found to be monoclinic, space group $P2_1/a$, with two molecules per unit cell located at inversion centers. The crystals of the α phase grow twinned, and only the parameters of the triclinic unit cell were determined by x-ray diffraction.[22] The atomic positions were obtained from packing calculations and the results are supported by spectroscopic evidence; the two molecules in the unit cell are located at symmetry unrelated inversion sites.[4] The optical frequencies for both phases have been calculated previously, and show good agreement with experiment (see Table I).

In contrast with *p*-dichlorobenzene the 1, 2, 4, 5-tetrachlorobenzene crystal shows an extremely sharp phase transition, with no metastable states, and therefore provides a counterexample to the case discussed in the previous section.

Taking into account the success of the Debye–Einstein approximation for *p*-dichlorobenzene it was used to calculate the thermodynamic functions of 1, 2, 4, 5-tetrachlorobenzene in the temperature range 100–300 K (see Fig. 4).

Table IV shows the calculated values of the internal energy, free energy, entropy, specific heat, and heat of sublimation for this compound at temperatures near the phase transition; unfortunately, there are no experimental data to check their accuracy. In this case the entropic contribution to the heat of sublimation is only about 8%. Figure 5 shows the free energy vs. temperature plots for both phases near the transition. It can be seen that the curves have a well defined crossing point near 200 K, to be compared with the transition temperature of 188 ± 2 K. This result is surprisingly accurate, since given the approximations involved in the calculation we would have expected only qualitative agreement.

CONCLUSIONS

In the present work we have calculated thermodynamic properties of two phases of *p*-dichlorobenzene and 1, 2, 4, 5-tetrachlorobenzene, using an intermolecular potential of the atom–atom type; in particular, we have observed the behavior of the free energy in the vicinity of

TABLE IV. Calculated thermodynamic functions of α- and β-1, 2, 4, 5-$C_6H_2Cl_4$. For definitions see Table III.

		Phase	
		α	β
Function	Units	180 K	200 K
E_{pack}		−18.81	−17.78
E_{lat}		2.18	2.41
E_{int}		39.55	39.90
E		22.92	24.53
	kcal/mole		
A_{lat}		−2.16	−3.33
A_{int}		39.01	39.26
A		18.04	18.15
ΔH_{sub}		17.76	16.66
S_{lat}		24.13	28.70
S_{int}		3.01	3.18
S		27.14	31.88
	cal/mole K		
$C_{v,lat}$		11.74	11.82
$C_{v,int}$		16.64	18.15
C_v		28.38	29.97

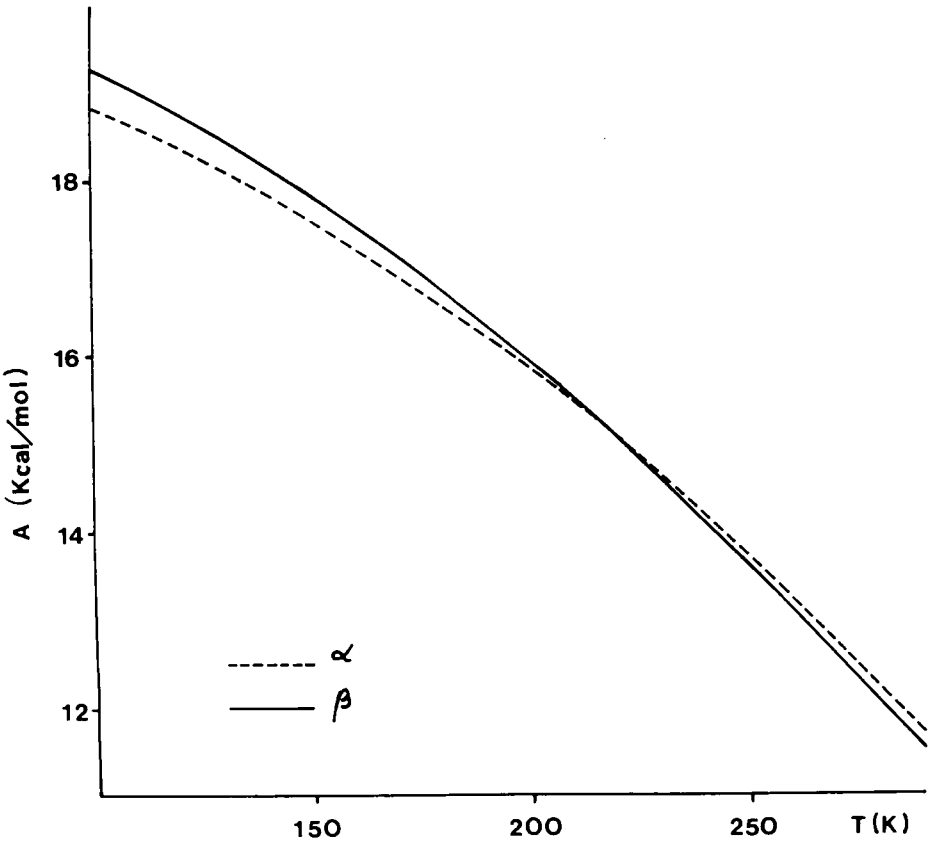

FIG. 5. Free energy vs temperature curves for α- and β-1, 2, 4, 5-$C_6H_2Cl_4$.

the phase transitions. There are several important points which have resulted from this investigation:

(i) The calculations are consistent with the experimental data. The free energies of both phases of *p*-dichlorobenzene are almost coincident, which is consistent with the fact that the phases are metastable, and the free energy curves for 1, 2, 4, 5-tetrachlorobenzene cross at a temperature which is very near the transition temperature, in coincidence with the well defined transition behavior.

(ii) For *p*-dichlorobenzene the Debye–Einstein approximation to the density of states is sufficiently accurate for the calculation of thermodynamic properties; this fact, together with its success for the cases of α- and γ-N_2, suggests that it could be extended to other molecular crystals as a simple tool to avoid cumbersome calculations.

(iii) The entropic contributions to the heat of sublimation are by no means negligible, and should be taken into account in future potential parameter fittings.

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