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A thermodynamic investigation of dynamical disorder in Phase II of CBr_4

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CBr_4 is an archetypal example of a pseudospherical molecule that can form an orientationally disordered phase (phase I, 320 K$<T<$365 K). At lower temperatures, phase II is the stable phase; although it must be more ordered than phase I, different techniques give conflicting results concerning order in phase II. In order to investigate dynamical disorder in phase II, the heat capacity of CBr_4 has been measured in the temperature range 30–305 K. No phase transitions were found in this region. The calculated heat capacity, with contributions due to low-frequency translation and rotational-vibrations of the rigid CBr_4 molecules, as well as internal motions, fits the experimentally derived C_v data to within 3%. Virtually full excitation of rigid molecule rotation-vibrations at very low temperatures (~45 K) is consistent with the observation of a low-temperature elevation in the calculated Grüneisen parameter. © *1995 American Institute of Physics.*

I. INTRODUCTION

In the solid state carbon tetrabromide is a molecular solid. Under its saturated vapor pressure it exists in two forms; an orientationally disordered face-centered-cubic structure with four molecules in the unit cell[1] (phase I, which exists between $T=320$ K and the melting point at $T=365$ K), and another phase (phase II) below 320 K.[2,3] Phase II has a monoclinic structure with 32 molecules in the unit cell (four independent molecules in the asymmetric unit).[4,5] It has been shown that the center-of-mass structures of these two solid phases are related, and the monoclinic structure is pseudo-cubic.[4] CBr_4 has two additional high-pressure phases.[6,7]

The dynamics of CBr_4 in phase I have been extensively studied, as this phase can be considered to be representative of an orientationally disordered solid. For example, its entropy of fusion[3,8] of 1.31 R, where R is the gas constant, is within Timmermans' defining limit for an orientationally disordered solid,[9] $\Delta_{fus}S<2.5R$. Furthermore, in contrast with some of the lighter pseudospherical molecules such as CH_4 that can show orientational polymorphism, CBr_4 can be treated classically. Lattice dynamics of CBr_4 also have been of interest owing to the role of rotational-translational coupling in the collective excitations of the crystal lattice. The simplified picture of the molecular motion of phase I of CBr_4 is that of six different molecular orientations, with each molecule undergoing discrete jumps between these positions.[10] However, molecular dynamics simulations indicate much more complex behavior with a wider range of orientations and additional sporadic free spinning.[11,12]

Although entropy considerations would indicate that phase II is more ordered than phase I, there is evidence that phase II is not fully ordered. For example, a ^{13}C NMR study of phase II detected molecular motion at 240 K,[13] well below the I→II phase transition. On the basis of thermal conductivity measurements of CBr_4, it has been concluded[14] that there is structural disorder in phase II. It also has been suggested that some molecules (with sufficiently high kinetic energy) might experience jumps at temperatures just below 320 K in phase II.[11] Furthermore, an analysis of the high-temperature heat capacity of CBr_4 led to the conclusion that there is essentially no change in the molecular motion at the II→I transition.[8]

We report here experimentally determined heat capacities of CBr_4 in phase II, from 30 K to 305 K. The simplicity of solid CBr_4 and the level of knowledge of other properties for this material make it possible to use the heat capacity data to quantify dynamical disorder in phase II of CBr_4. In addition, with the present results there is sufficient experimental information for this system to calculate related thermodynamic properties, viz., isobaric heat capacity and the Grüneisen parameter.

II. EXPERIMENTAL METHODS

CBr_4 was obtained from Aldrich at a stated purity of 99%. It was then sublimed to further remove impurities. This method was reported to be more effective for purification of CBr_4 than recrystallization from solution.[8] The mass of the sample used in the calorimetric experiments was 9.2904 g.

The heat capacity of CBr_4 was measured in the temperature range from 30 K to 305 K by means of an adiabatic heat-pulse calorimeter. The apparatus and the procedure have been described in detail elsewhere.[15,16] Briefly, this method is based on measurement of the absolute value of the total heat capacity of the sample and the sealed calorimetric vessel through the determination of the temperature increment in response to a quantified energy provided to the system while maintaining adiabatic conditions. Through knowledge of the predetermined heat capacity of the empty calorimetric vessel as a function of the temperature, the heat capacity of the sample was determined. Previous measurements of the heat capacity of Calorimetric Conference (NBS-49) benzoic acid agreed with the literature values[17] to within 0.5% for this apparatus.[16]

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TABLE I. Smoothed values of isobaric heat capacity, $C_P(=C_{sat})$, and isochoric heat capacity, C_V, for CBr_4. Both sets of values are expressed in terms of the gas constant, $R(=8.314\ J\ K^{-1}\ mol^{-1})$.

T/K	C_P/R	C_V/R
30	4.97	4.93
35	5.70	5.65
40	6.21	6.13
45	6.62	6.52
50	7.04	6.91
55	7.43	7.28
60	7.76	7.57
65	8.11	7.88
70	8.41	8.15
75	8.72	8.42
80	9.04	8.71
85	9.33	8.96
90	9.59	9.17
95	9.84	9.38
100	10.07	9.57
110	10.45	9.89
120	10.76	10.13
130	11.09	10.40
140	11.33	10.58
150	11.58	10.79
160	11.84	11.00
170	12.09	11.21
180	12.35	11.44
190	12.59	11.64
200	12.88	11.89
210	13.18	12.14
220	13.45	12.34
230	13.69	12.51
240	13.98	12.69
250	14.24	12.82
260	14.55	12.96
270	14.85	13.03
280	15.20	13.08
290	15.58	13.06
300	15.98	12.97

III. RESULTS AND DISCUSSION

A. Experimental findings

In all, there were 243 independent determinations of the heat capacity of CBr_4 in this temperature range. The heat capacity of CBr_4 contributed ~50% to the total heat capacity at the lowest temperatures, decreasing to ~40% at the highest temperatures. The compound behaved well thermally. No thermal history effects, which can indicate properties such as frozen disorder, were observed. The relaxation times after heating, which slightly decreased at lower temperatures, did not exceed 15 min.

Smoothed values of the experimental molar heat capacity under saturated vapor, C_{sat}, are given in Table I. The experimental results are shown in Fig. 1. The heat capacity as a function of temperature is smooth with no singularities due to phase transitions in the temperature range of 30–305 K, extending the conclusion of earlier differential scanning calorimetry results (which had been carried out down to 115 K).[18] The heat capacity of CBr_4 reported previously[8] above 295 K is also shown in Fig. 1, and agreement with the present results is within experimental error.

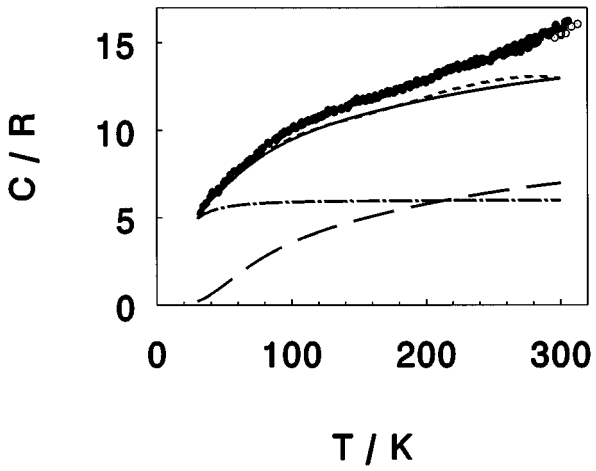

FIG. 1. Heat capacity as a function of temperature for CBr_4. ●, present experimental C_{sat} data; ○, experimental C_{sat} data from Ref. 8; ---, C_V derived from experimental C_{sat}; – – –, C_V^{int} calculated as described in the text; – – –, C_V^{ext} calculated as described in the text; —, calculated C_V $(=C_V^{int} + C_V^{ext})$. All heat capacities are expressed in terms of the gas constant, $R(=8.314\ J\ K^{-1}\ mol^{-1})$.

B. Isochoric heat capacity, C_v

The heat capacities determined in the experiment are the heat capacities of the solid in equilibrium with its saturated vapor, i.e., C_{sat}, which is related to the isobaric heat capacity, C_P, by[19]

$$C_{sat}=C_P-T\left(\frac{\partial P}{\partial T}\right)_{sat}\left(\frac{\partial V}{\partial T}\right)_P, \tag{1}$$

where V is the volume of the solid and P is the pressure. For nonvolatile solids $(\partial P/\partial T)_{sat}\simeq 0$ and therefore $C_{sat}\simeq C_P$. The isochoric heat capacity, C_V, can be obtained from the measured heat capacity if the following thermodynamic relation is employed:[19]

$$C_P=C_V+TV_m\frac{\alpha_V^2}{\beta_T}, \tag{2}$$

where V_m is the molar volume of the sample, α_V is the volume thermal expansion $[\alpha_V=(\partial \ln V/\partial T)_P]$, and β_T is the isothermal compressibility $[\beta_T=-(\partial \ln V/\partial P)_T]$. Strictly speaking, Eq. (2) conveys less information when applied to anisotropic materials and therefore the tensorial form should be used here since phase II of CBr_4 is monoclinic; however, this phase is pseudocubic[4] and therefore Eq. (2) was used. Values of the thermodynamic variables required to calculate C_V from C_P for CBr_4 are not available for the whole temperature range of the experimental heat capacity data. However, the thermal expansion of CBr_4 is known[20] in the temperature range from 210 K to 320 K (and we have extrapolated it to lower temperatures) and the isothermal compressibility is known[8] at 273 K and 310 K. This allowed us to calculate C_V within about ±2%. The smoothed values of the isochoric heat capacity are given in Table I. These values are shown in Fig. 1.

The degrees of freedom which can be excited thermally in a molecular solid, giving rise to the temperature-dependence of the heat capacity, can be understood as fol-

lows. Each molecule can have internal motions associated with its normal modes of vibration, and external modes associated with whole-molecule translations and whole-molecule rotational-vibrations. The internal modes are observable with optical spectroscopic techniques; for CBr_4 these modes are all Raman active and they have been fully assigned.[21] The contribution of these modes to the heat capacity will be well-described by the Einstein model; this contribution is shown in Fig. 1, as C_V^{int}. At the lowest temperature measured, 30 K, the remaining portion of C_V (i.e., $C_V - C_V^{\text{int}}$) is already 80% of its maximum possible value, $6R$, and this proportion increases rapidly to 95% by 45 K. On this basis, and with Raman experiments showing[21] the lattice modes to fall in the frequency range from 15 to 49 cm^{-1}, the external modes were approximated as a three-dimensional Einstein oscillator of characteristic temperature $\theta_E = 60$ K and a three-dimensional Debye oscillator of characteristic temperature $\theta_D = 60$ K. (These values, which are upper limits as lower-temperature heat capacity data would be required to determine θ_E and θ_D accurately, are comparable with $\theta_E = 68$ K and $\theta_D = 64$ K for $CBrCl_3$ and $\theta_E = 62$ K and $\theta_D = 58$ K for CBr_2Cl_2.[22]) This external mode contribution, C_V^{ext}, is shown in Fig. 1, where the calculated temperature-dependence of C_V can be seen to compare very favorably with the temperature-dependence of C_V derived from the measured heat capacities; the maximum difference between them is less than 3%.

C. Grüneisen parameter

Intermolecular forces determine many properties of molecular crystals, particularly thermal and mechanical properties, since they define the character of the potential between the constituent chemical species. Knowledge of the spatial as well as the harmonic/anharmonic character of the intermolecular interaction is crucial to understanding lattice dynamics and their consequences. The Grüneisen parameter has been useful in aiding understanding of anharmonic properties of solids, especially those displaying significant long-range interactions, as in ionic crystals.[23] To date, Grüneisen parameters of molecular crystals have not been investigated so extensively,[23] although there are recent reports for inclusion compounds[24] and C_{60}.[25] Thus, now we turn our attention to anharmonic properties of CBr_4 since relevant values of the thermal properties are available to quantify this.

The overall Grüneisen parameter, γ, appears naturally in the equation of state in the quasi-harmonic approximation and is given by[19]

$$\gamma = \frac{\alpha_V V}{\beta_T C_V} = \frac{\alpha_V V}{\beta_S C_p}, \tag{3}$$

where β_S is the adiabatic compressibility. In principle the overall Grüneisen parameter is related to the anharmonic behavior of a crystal potential through the mode Grüneisen parameters[19,23] γ_{ik} ($\gamma = \Sigma_{ki}\gamma_{ki}C_{ki}/\Sigma_{ki}C_{ki}$, where $\gamma_{ki} = -\partial \ln \omega_{ki}/\partial \ln V$; the sum is taken over the all modes in the first Brillouin zone, and ω_{ki} and C_{ki} are the frequency of the particular normal mode and its contribution to the heat capacity, respectively). Thus, from the microscopic viewpoint, any unusual thermal expansion behavior is due to peculiarities in the behavior of the Grüneisen parameter.

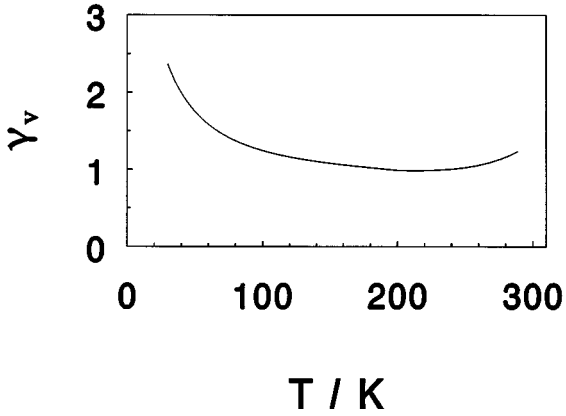

FIG. 2. The volume Grüneisen parameter, γ_v, for CBr_4 as a function of temperature.

The Grüneisen parameter for phase II CBr_4 as a function of temperature, derived from the present data for C_V, is shown in Fig. 2. The values of γ are comparable to those characteristic for nonmetallic solids with γ of the order of unity.[23] Although for most materials γ decreases with decreasing temperature ($\gamma \to 0$ as $T \to 0$ due to increasing harmonicity), for CBr_4 there is a low-temperature elevation of γ. The same trend was observed for other substances such as Dianin's inclusion compounds,[24] tetrahydrofuran clathrate hydrate,[26] and disordered materials and crystals doped with impurities.[23] In solid carbon monoxide this elevation was attributed to the presence of low-frequency librational modes,[23] which also can be the case for phase II of CBr_4.

It is worth noting a *caveat* concerning the physical meaning of the overall Grüneisen parameter in the case of molecular crystals. The strain and stress for these materials can be split into external components (due to the displacement of points of the ideal Bravais lattice) and internal components (due to relative placement of atoms and molecules in the unit cell to minimize the interaction energy).[27,28] Internal strains redress the lattice strain through energy redistribution.[28] Ideally the Grüneisen parameter calculation would be based on the mode γ determination (although there is insufficient data to carry out this calculation for CBr_4). The thermodynamics of internal strains[27] are nontrivial for a material with a wide range of internal vibrations, e.g., CBr_4. This can significantly affect the values of γ's, obfuscating the physical meaning of this parameter, e.g., the mode γ's due to internal modes might be anomalously small despite strong anharmonicity of these modes.[27,29] The same was postulated for the modes due to rigid-molecule librations.[30] Since both internal and external modes are present in CBr_4, the temperature evolution of the calculated γ would be influenced by any coupling between internal and external modes.

D. Disorder in phase II

The picture of phase II that emerges from this investigation is that of a molecular solid in which the external modes (translation and rotational-vibrations of the rigid CBr_4 mol-

ecules) are virtually fully excited at temperatures as low as 45 K. At higher temperatures the major contribution to the temperature-dependence of the isochoric heat capacity is due to thermal excitation of internal degrees of freedom.

On this basis it is clear why the NMR experiment[13] detected significant molecular motion in phase II. Whereas in some molecular solids NMR results can indicate pretransitional effects far below the temperature of the phase transition,[31,32] this appears not to be the case here; the detected motion is an intrinsic feature of phase II of CBr_4. Although thermal conductivity results for phase II of CBr_4 have been interpreted in terms of structural disorder,[14] it would appear that the structure is ordered but the rotational-vibrations of the molecules are fully excited at relatively low temperatures. This is consistent with NQR results;[33] disappearance of the NQR signal somewhere above 80 K probably results from these degrees of freedom.

This view of phase II of CBr_4 is supported by the Grüneisen parameter results presented here. The elevation of the Grüneisen parameter in the low-temperature region could be attributed to low-frequency rotation-vibrational motions of the CBr_4 molecules and the associated high degree of anharmonicity of the intermolecular potential.

E. Comments concerning phase I

What do these conclusions concerning phase II imply for phase I of CBr_4? Given the large entropy change[8] ($\Delta_{II\rightarrow I}S = 2.51\ R$), phase I is more disordered than phase II, but thermodynamics[8] indicate that the types of rotation-vibrational motions are not greatly changed as a result of the II→I transition. From NMR experiments it was found[13,34] that the time scale of the whole-molecule jump motion changes from about 1 ns at 20 °C in phase II to about 10 ps at 50 °C in phase I. In addition to the change in jump time, diffuse neutron scattering,[10,35,36,37] simulations,[12] and Brillouin scattering[38] indicate the important role of steric interactions and rotational-translational coupling in Phase I of CBr_4.

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