

# Specific Heat of Molecular Crystals from Atomic Mean Square Displacements with the Einstein, Debye, and Nernst–Lindemann Models

Thammarat Aree<sup>†,‡</sup> and Hans-Beat Bürgi<sup>\*,†</sup>

Laboratorium für Chemische und Mineralogische Kristallographie, Universität Bern, Freiestrasse 3, CH-3012 Bern, Switzerland, and Department of Chemistry, Faculty of Science, Chulalongkorn University, Phayathai Road, Pathumwan, Bangkok 10330, Thailand

Received: June 11, 2006; In Final Form: October 4, 2006

Analysis of atomic displacement parameters (ADPs) from multitemperature diffraction data provides mean-field molecular translation and libration frequencies. These quantities have been combined with molecular deformation frequencies calculated *ab initio*, e.g. by DFT methods, to calculate the specific heat  $C_v$  of molecular crystals of naphthalene, anthracene, and hexamethylenetetramine. If the difference  $C_p - C_v$  is represented by the Nernst–Lindemann relation,  $C_p$  curves from diffraction experiments and *ab initio* calculations agree well with those based on calorimetry. Agreement is better if the Debye rather than the Einstein model is chosen to represent the contribution of the translational vibrations. Compressibilities estimated from the differences  $C_p - C_v$  are 2–5 times higher than those obtained from compressibility measurements at 298 K and Grüneisen constants derived from the temperature dependence of ADPs.

## 1. Introduction

Atomic motion in crystals is evident from the atomic displacement parameters (ADPs) determined routinely in every crystal structure analysis and from the temperature dependence of these parameters. Almost exactly 50 years ago Cruickshank predicted the variation of the molecular vibration amplitudes with temperature in benzene, naphthalene, and anthracene from X-ray and Raman studies.<sup>1</sup> Cruickshank also calculated the entropy of naphthalene using characteristic frequencies derived from X-ray and spectroscopic analyses.<sup>2</sup> In the meantime electronic area detectors have accelerated diffraction measurements by orders of magnitude. Due to extensive software development and nearly unlimited computer resources improved data interpretation and high-quality quantum mechanical calculations have become available. Encouraged by these advances and by recent adaptations of the theoretical framework (see next paragraph), we have reinvestigated the possibility of combining results from diffraction experiments with those from quantum mechanical calculations to obtain specific heat curves for crystalline materials.

In this work we determine the low-frequency vibrational contribution to the specific heat of molecular crystals from elastic, single-crystal diffraction experiments. The necessary information is contained in the temperature evolution of ADPs.<sup>3</sup> The models of motion developed to interpret ADPs account explicitly for the six low-frequency, external vibrations (three molecular translations and three librations) and implicitly for high-frequency, internal vibrations (molecular deformations). The general relationship takes the form of a harmonic normal-mode analysis based on ADPs:

$$\Sigma^x(T) = \mathbf{A} \mathbf{g} \mathbf{V} \delta(T) \mathbf{V}^T \mathbf{g}^T \mathbf{A}^T + \epsilon^x \quad (1)$$

where  $\delta(T)$  is a diagonal matrix with elements

$$\delta_i(T) = \frac{h}{8\pi^2 \nu_i} \coth\left(\frac{h\nu_i}{2kT}\right) \quad (2)$$

The matrices  $\mathbf{g}$  and  $\mathbf{A}$  transform the normal modes with frequencies  $\nu_i$  and eigenvectors  $\mathbf{V}$  into atomic displacements  $\Sigma^x(T)$ ; ADPs are the  $3 \times 3$  diagonal blocks of  $\Sigma^x$ ;  $\epsilon^x$  is a temperature-independent term accounting for the high-frequency vibrations, which are not significantly excited in the temperature range of the diffraction experiment;  $h$  is the Planck constant; and  $k$  is the Boltzmann constant. The parameters of the model, i.e., the frequencies  $\nu_i$ , the independent elements of the orthonormal matrix  $\mathbf{V}$  representing molecular displacement coordinates and the six independent elements of each of the  $3 \times 3$  diagonal blocks of  $\epsilon^x$ , are determined by a least-squares procedure from the multitemperature ADPs. Note that the information from ADPs pertaining to a single temperature is insufficient to perform such a normal-mode analysis.<sup>3</sup>

With the help of this novel approach we have analyzed the zero-point vibrational amplitudes of benzene,<sup>4,5</sup> isotope effects in crystalline benzene and perdeuterobenzene,<sup>6</sup> the librational and translational motions of naphthalene,<sup>7,8</sup> anthracene,<sup>7</sup> and hexamethylenetetramine (HMT)<sup>9</sup> and the out-of-plane deformation of the peptidic  $\text{NH}_2$ -groups of urea.<sup>4</sup> For naphthalene and HMT the specific heat  $C_v$  has been calculated from the 6 external frequencies derived by ADP analysis and from the  $3n - 6$  internal frequencies calculated *ab initio*.<sup>8,9</sup> There are noticeable differences between  $C_v$  calculated from ADPs and  $C_p$  measured by calorimetry. The main discrepancies are found in the low-temperature range ( $< 100$  K) and around room temperature. At low temperature  $C_v$  as well as  $C_p$  depends primarily on the external vibrations and on the structure of the vibrational density of states. At room temperature most of the difference arises from the different definitions of  $C_v$  and  $C_p$ .

The temperature dependence of the ADPs also reveals an anharmonic effect associated with the thermal expansion of the crystal. The latter diminishes the crystal field with increasing temperatures, decreases the external vibration frequencies, and causes the ADPs to increase faster than linear in temperature.

\* Address correspondence to this author. Phone: +41-31-631-4281. Fax: +41-31-631-3996. E-mail: hans-beat.buergi@krist.unibe.ch.

<sup>†</sup> Universität Bern.

<sup>‡</sup> Chulalongkorn University.

This effect can be clearly discerned experimentally and expressed in terms of the volume dependence of the external frequencies  $\Delta\nu_i/\nu_i(0) = -\gamma_{G,i}\Delta V(T)/V(0)$ . The proportionality factors  $\gamma_{G,i}$  are called Grüneisen constants<sup>10</sup> and may also be derived from the temperature dependence of the ADPs.<sup>9</sup>

In the present work, we calculate  $C_p(T)$  from results of diffraction experiments and ab initio calculations and compare it with  $C_p(T)$  measured by calorimetry. The former quantity, or rather its relative  $C_v(T)$ , is alternatively calculated with an Einstein model for all external and internal frequencies or with a Debye model for the 3 translation frequencies and an Einstein model for the remaining  $3n - 3$  frequencies.  $C_p(T)$  is calculated from  $C_v(T)$  either by taking into account experimental measurements and estimates of crystal compressibility or by using the empirical Nernst–Lindemann model.<sup>11</sup> The comparison is illustrated by a number of examples, namely naphthalene, anthracene, and HMT.

## 2. The Model

**2.1. Debye Frequencies from Einstein Frequencies.** There are two simple models for describing lattice vibrations: first, the Einstein model, which neglects the interatomic interactions and assumes that all atoms are identical and vibrate at the same frequency; second, the Debye model, which considers collective atomic motions in terms of a simplified, analytical distribution of vibrational frequencies. The vibrational density of states  $g_E(\nu)$  underlying the molecular Einstein model consists of  $3n$  delta functions,

$$g_E(\nu) = \begin{cases} \delta, & \nu = \nu_{E,i} \\ 0, & \nu \neq \nu_{E,i} \end{cases} \quad (i = 1, 2, 3, \dots, 3n) \quad (3)$$

where  $\nu_{E,i}$  is a molecular vibration frequency and  $n$  the number of atoms in the molecule. The delta functions are usually sufficient for representing the narrow dispersion of the 3 rotational and  $3n - 6$  internal deformation modes, but not for the much wider dispersion of the 3 translational modes. Therefore, the latter are described with the more realistic Debye frequency distribution as

$$g_D(\nu) = \begin{cases} 3\nu^2/\nu_{D,i}^3, & \nu < \nu_{D,i} \\ 0, & \nu > \nu_{D,i} \end{cases} \quad (i = 1, 2, 3) \quad (4)$$

where  $\nu_{D,i}$  is a Debye frequency. In the low-temperature, zero-point regime the ADPs are proportional to the inverse frequencies, and in the high-temperature, classical regime to the inverse square of the frequencies (eq 2). For this reason inverse Debye frequencies have been estimated from inverse Einstein frequencies for both regimes.

$$\int_0^{\nu_D} \frac{1}{\nu} g_D(\nu) d\nu = \frac{1}{\nu_E} \quad (5)$$

$$\int_0^{\nu_D} \frac{1}{\nu^2} g_D(\nu) d\nu = \frac{1}{\nu_E^2} \quad (6)$$

The Debye frequencies are 1.5 and 1.732 times the respective Einstein frequencies in the quantum and classical limits, respectively.

**2.2. Calculation of  $C_v$ .** The molar contribution to  $C_v$  from external vibrations is obtained by using the Debye model of heat capacity for the 3 translational frequencies and the Einstein model for the 3 librational and the  $3n - 6$  internal frequencies

$$C_v(T) = \sum_{i=1}^3 3R \left( \frac{T}{1.437\bar{\nu}_{D,i}} \right)^3 \int_0^{1.437\bar{\nu}_{D,i}/T} \frac{x^4 e^x}{(e^x - 1)^2} dx + \sum_{i=4}^6 R \left( \frac{1.437\bar{\nu}_{E,i}}{T} \right)^2 \frac{e^{1.437\bar{\nu}_{E,i}/T}}{(e^{1.437\bar{\nu}_{E,i}/T} - 1)^2} + \sum_{i=7}^{3n} R \left( \frac{1.437\bar{\nu}_{\text{int},i}}{T} \right)^2 \frac{e^{1.437\bar{\nu}_{\text{int},i}/T}}{(e^{1.437\bar{\nu}_{\text{int},i}/T} - 1)^2} \quad (7)$$

where  $\bar{\nu}_{D,i}$  and  $\bar{\nu}_{E,i}$  are Debye and Einstein frequencies (in  $\text{cm}^{-1}$ ), respectively;  $\bar{\nu}_{\text{int},i}$  are frequencies of intramolecular vibrations;  $n$  is the number of atoms per molecule; and  $R$  is the gas constant,  $1.987 \text{ cal K}^{-1} \text{ mol}^{-1}$ .

**2.3. Calculation of  $C_p$ .** The molar specific heat  $C_p$  is

$$C_p(T) = C_v(T) + T\chi^2(T)V(T)/\kappa(T) \quad (8)$$

where  $\chi(T)$  is the thermal expansivity,  $V(T)$  the molar volume, and  $\kappa(T)$  the compressibility. The thermal expansion and the molar volume are available from the diffraction experiments, which provide not only ADPs, but also unit cell constants and their temperature dependence. Experimental values of compressibility are often known for specific temperatures only or are not available at all. This lack of information complicates obtaining  $C_p$  for the full temperature range of the diffraction data. We have followed three routes to estimate the difference between  $C_v$  and  $C_p$ . The first one is to use experimental values of the compressibility. The second is to estimate the compressibility function  $\kappa_G(T)$  and thus the difference  $C_p - C_v$  from the thermodynamic Grüneisen parameter  $\gamma_{G,\text{th}}$  (ref 10)

$$\kappa_G(T) = \frac{\chi(T)V(T)}{\gamma_{G,\text{th}}C_v(T)} \quad (9)$$

$$C_p(T) - C_v(T) = \gamma_{G,\text{th}}T\chi(T)C_v(T) \quad (10)$$

For purposes of comparison,  $\kappa(T)$  may also be evaluated from the difference between  $C_v(T)$  calculated from ADPs and  $C_p(T)$  measured by calorimetry (eq 8). The third possibility is to exploit the original, empirical Nernst–Lindemann relation,<sup>11</sup> i.e., the equation in which  $C_v(T)$  has not been approximated by  $C_p(T)$ . In the form written by Pan et al.<sup>12</sup> it is

$$C_p(T) - C_v(T) = 3RA_0 \frac{TC_v(T)}{T_m} \quad (11)$$

$T_m$  is the melting point and the quantity  $A_0$  is claimed to be a universal constant,<sup>12</sup>  $1.63 \times 10^{-2} \text{ K mol cal}^{-1}$ .

## 3. The Data

**3.1. Librations, Translations, and Grüneisen Constants from ADPs.** Multitemperature diffraction data of naphthalene, anthracene, and HMT have been collected and analyzed by various authors.<sup>7–9,13–17</sup> For naphthalene, there are three recent sets of ADPs which were analyzed for normal modes by Capelli, Albinati, Mason, and Willis:<sup>8</sup> set 1 is from sealed-tube data to  $0.43 \text{ Å}$  resolution at 100, 135, 170, and 205 K refined with an anisotropic multipolar atom model by Oddershede and Larsen;<sup>13</sup> the resulting residual density maps are flat and featureless, thus suggesting that the ADPs obtained are not biased from the bonding density; set 2 is from synchrotron data to  $0.57 \text{ Å}$  resolution at 10, 30, 60, 90, 120, 150, 180, and 220 K refined with an anisotropic spherical atom model;<sup>8</sup> set 3 is from neutron

**TABLE 1: Low-Frequency External Vibrations and Summary of High-Frequency Internal Vibrations for Naphthalene, Anthracene, and HMT**

| compd   | external vibrations from multitemperature ADPs |                                     |  | internal vibrations from DFT calcn (spectro) <sup>a</sup> |                        |
|---|--|-------------------------------------|--|---|------------------------|
|   | temp <sup>b</sup> (K)                          | radiation <sup>b</sup> [refinement] | freq <sup>c</sup> ( $\bar{\nu}_{E,i}$ , cm <sup>-1</sup> ) | no. of freq   | freq range             |
| naphthalene<br>C <sub>10</sub> H <sub>8</sub>         | 100, 135, 170,                                 | sealed-tube <sup>13</sup>           | 108/73.0/54.7  | 48  | 171–3185<br>(176–3060) |
|   | 205  | [multipole]                         | 43.9/50.5/52.8   |   |                        |
|   | 10, 30, 60, 90,                                | synchrotron <sup>8</sup>            | 109/74.1/53.8  |   |                        |
|   | 120, 150, 180, 220                             | [spherical]                         | 41.9/47.7/50.0   |   |                        |
|   | 5, 30, 80, 150,                                | neutron <sup>8</sup>                | 110/75.4/56.7  |   |                        |
| anthracene<br>C <sub>14</sub> H <sub>10</sub>         | 220, 295                                       | [spherical]                         | 43.8/49.4/53.5   | 66  | 97–3185<br>(106–3048)  |
|   | 94, 140, 181,                                  | sealed-tube <sup>16</sup>           | 112/69.1/47.6  |   |                        |
|   | 220, 259, 295                                  | [multipole] <sup>15</sup>           | 36.2/43.4/46.4   |   |                        |
| HMT<br>(CH <sub>2</sub> ) <sub>6</sub> N <sub>4</sub> | 15, 50, 80,                                    | neutron <sup>15</sup>               | 48.9/48.9/48.9   | 60  | 374–3085<br>(378–2955) |
|   | 120, 160, 200                                  | [spherical]                         | 49.6/49.6/49.6   |   |                        |

<sup>a</sup> Internal frequencies from DFT calculations at the level B3LYP/6-311+G(2d,p)<sup>19</sup> in the gas phase and from spectroscopy in the solid phase for naphthalene,<sup>20</sup> anthracene,<sup>21–23</sup> and HMT.<sup>24</sup> Complete lists of frequencies are given as Supporting Information. <sup>b</sup> Temperatures of diffraction experiments, radiation used, and models of structure refinement. <sup>c</sup> The sequence of six Einstein frequencies  $\bar{\nu}_{E,i}$ : librations  $\bar{\nu}(l_x)$ ,  $\bar{\nu}(l_y)$ ,  $\bar{\nu}(l_z)$  and translations  $\bar{\nu}(t_x)$ ,  $\bar{\nu}(t_y)$ ,  $\bar{\nu}(t_z)$ . For Debye translational frequencies,  $\bar{\nu}_{D,i} = 1.616\bar{\nu}_{E,i}$ .

data to 0.63 Å resolution at 5, 30, 80, 150, 220, and 295 K refined with an anisotropic atom model.<sup>8</sup> We do not consider here the earlier results by Brock, Dunitz, and Hirshfeld, which cover a smaller temperature range and are of more limited resolution,<sup>14,15</sup> nor a later normal-mode analysis of their ADPs.<sup>7</sup> For anthracene, sealed-tube data to 0.77 Å resolution at 94, 140, 181, 220, 259, and 295 K were collected by Brock and Dunitz,<sup>16</sup> refined by Brock, Dunitz, and Hirshfeld<sup>15</sup> with an anisotropic multipole atom model using deformation densities transferred from perylene and analyzed for normal modes by Bürgi, Rangavittal, and Hauser.<sup>7</sup> Note that the ADPs of anthracene decrease by up to three times their s.u.'s upon replacing the spherical atom by the multipole atom models.<sup>15</sup> For HMT, neutron data to 0.64 Å resolution were collected at 15, 50, 80, 120, 160, and 200 K and refined by Kampermann, Sabine, and Craven.<sup>17</sup> Their results were analyzed for normal modes by Bürgi, Capelli, and Birkedal.<sup>9</sup>

Experimental temperatures and external Einstein frequencies obtained from normal-mode analysis of the ADPs are summarized in Table 1. The sequence of six frequencies is the following: librations  $\bar{\nu}(l_x)$ ,  $\bar{\nu}(l_y)$ ,  $\bar{\nu}(l_z)$  and translations  $\bar{\nu}(t_x)$ ,  $\bar{\nu}(t_y)$ ,  $\bar{\nu}(t_z)$ , where  $x$ ,  $y$ , and  $z$  are the long, intermediate, and short axes of the naphthalene and anthracene molecules. For this work the frequencies and the Grüneisen constants of anthracene and HMT have been recalculated from the ADPs reported originally (see the Supporting Information).<sup>7,9</sup> In the new calculations  $V(T)$  has been expressed as a polynomial with 0th, 2nd, and 3rd order rather than 0th, 1st, and 2nd order terms in  $T$ . This change takes into account the thermodynamical boundary condition according to which the thermal expansivity must be zero at  $T = 0$  K. The recalculated frequencies differ only slightly from those given originally.<sup>7,9</sup> For the calculations the thermodynamic Grüneisen constant  $\gamma_{G,th}$  (eq 11), which is usually in the range 1–3, was taken to be the same as the vibrational  $\gamma_G$ , because the two quantities generally differ only by a few percent at elevated temperatures.<sup>18</sup> The values of  $\gamma_{G,th}$  are 2.9, 2.3, and 4.0 for naphthalene sealed-tube, synchrotron, and neutron data, 3.2 for anthracene, and 2.6 for HMT. The differences of the values of  $\gamma_{G,th}$  for naphthalene may seem puzzling. They are due to the fact that the three different experiments give slightly different results, especially for the ADPs. Among the results of a diffraction experiment ADPs are most susceptible to absorbing effects from imperfect integration of the primary diffraction data, absorption, and extinction corrections.

The two lowest calculated internal frequencies of anthracene overlap with the six external frequencies. They have been

determined from the ADPs together with the external ones and replace the two lowest frequencies calculated ab initio (see the Supporting Information).

**3.2. Internal Vibrations from ab Initio Calculations.** The frequencies of internal vibrations of naphthalene, anthracene, and HMT have been obtained from DFT calculations at the level B3LYP/6-311+G(2d,p) with program Gaussian98.<sup>19</sup> Since the calculated frequencies ( $\bar{\nu}_{calc}$ ) of the gaseous molecules tend to be overestimated compared with those from IR and Raman measurements ( $\bar{\nu}_{int}$ ) on solid naphthalene,<sup>20</sup> anthracene,<sup>21–23</sup> and HMT,<sup>24</sup> they have been scaled with a factor  $S$  obtained from averaging the ratio of  $\bar{\nu}_{int,i}/\bar{\nu}_{calc,i}$ , i.e.

$$S = \frac{1}{3n-6} \sum_{i=1}^{3n-6} \frac{\bar{\nu}_{int,i}}{\bar{\nu}_{calc,i}} \quad (12)$$

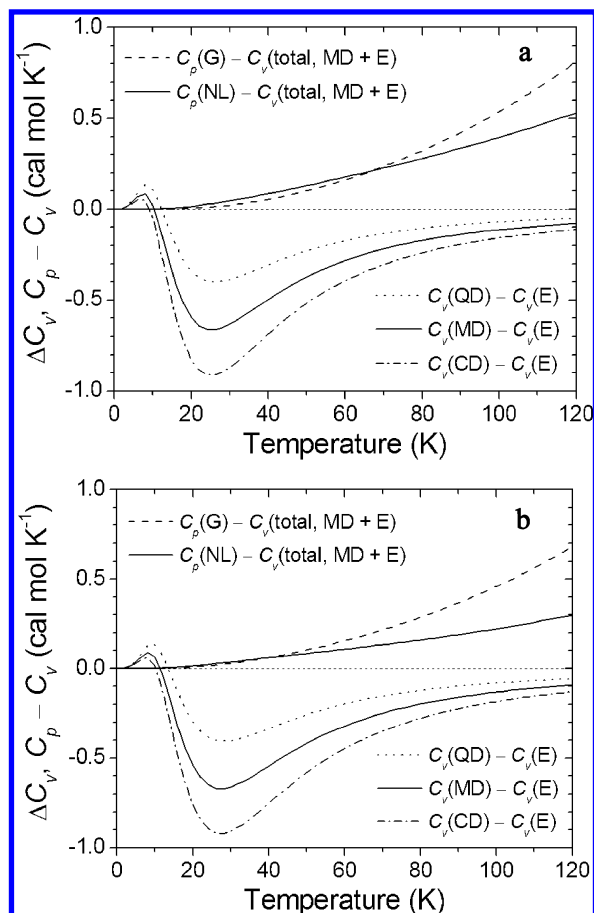
The number and ranges of calculated and measured frequencies of the three compounds are given in Table 1. The full lists of frequencies are given as Supporting Information. The scaling factors are 0.977, 0.987, and 0.982 for naphthalene, anthracene, and HMT, respectively, close to the values proposed by Scott and Radom.<sup>25</sup>

**3.3.  $C_p$  from Calorimetry.** The heat capacity  $C_p$  of naphthalene has been measured in different temperature ranges by various authors: Huffman et al. (91–295 K),<sup>26</sup> Southard and Brickwedde (15–295 K),<sup>27</sup> McCullough et al. (12–371 K),<sup>28</sup> and Chirico et al. (5–440 K).<sup>29</sup> The results of these authors are very similar; discrepancies between the last two experiments are less than 2% (0.03 cal mol<sup>-1</sup> K<sup>-1</sup>) below 30 K and less than 0.1% (0.04 cal mol<sup>-1</sup> K<sup>-1</sup>) in the temperature range 30 to 300 K. The measurement of Chirico et al.<sup>29</sup> covers the full temperature range of the diffraction data, is the most recent, and will be used for comparisons.  $C_p$  values of anthracene and HMT are taken from refs 30 and 31, respectively.

#### 4. Debye vs Einstein Frequencies—Influence of Compressibility

**4.1. Debye vs Einstein Frequencies.** Figure 1a,b shows the effect on  $C_v$  of replacing translational Einstein by Debye frequencies for the naphthalene synchrotron<sup>8</sup> and HMT neutron data<sup>9</sup> (eq 7).  $C_v$  from the Einstein model is higher than that from the Debye model in most of the temperature range to 120 K and by up to 25%. The effect is larger if the Debye frequencies are obtained from the classical rather than from the quantum approximations (eqs 5 and 6). It is difficult to specify





**Figure 1.** Differences between  $C_p$  obtained with the Einstein and Debye models of the three translational frequencies. The Debye frequencies have been estimated in the quantum (1.5, QD), classical (1.732, CD), and mean Debye limits (1.616, MD) (lower part of each frame). Differences between  $C_p$  estimated from the Nernst–Lindemann (NL) relation or Grüneisen constant (G) and  $C_p$  derived from the mean Debye model for translational frequencies and Einstein model for librational and internal frequencies (upper part of each frame). The effects are illustrated for (a) synchrotron data of naphthalene and (b) HMT data. For analogous information for sealed-tube X-ray and neutron data of naphthalene and for anthracene data, see the Supporting Information.

in which temperature range a given approximation dominates. For later comparisons of  $C_p$  calculated from ADPs with  $C_p$  from calorimetry we have therefore chosen to use the mean Debye value  $\bar{\nu}_{D,i} = 1.616\bar{\nu}_{E,i}$  (MD), which is the average of the quantum (QD, 1.5) and classical (CD, 1.732) limits. At higher temperatures the Einstein model and the Debye models become the same, namely  $3R$ .

**4.2. Influence of Compressibility.** Compressibility has been taken into account by using the Nernst–Lindemann relation,<sup>11</sup> eq 11, with  $A_0 = 1.63 \times 10^{-2} \text{ K mol cal}^{-1}$  (ref 12) or according to eq 10 with Grüneisen constants of 2.9, 2.3, and 4.0 for naphthalene sealed-tube, synchrotron, and neutron data, 3.2 for anthracene, and 2.6 for HMT. Corresponding differences  $C_p - C_v$  in the temperature range 0–120 K are shown for naphthalene synchrotron and HMT neutron data in Figure 1a,b; they amount to several tenths of a  $\text{cal mol}^{-1} \text{ K}^{-1}$  below 120 K and to several  $\text{cal mol}^{-1} \text{ K}^{-1}$  at room temperature. They are smallest if the Nernst–Lindemann relation is used, larger from the Grüneisen constants, and largest if the experimental compressibility values are invoked (not shown in Figure 1a,b). For later comparisons of  $C_p$  calculated from ADPs with  $C_p$  from calorimetry we have chosen to use  $C_p$  obtained with the Nernst–Lindemann relation.<sup>11</sup>

## 5. Discussion

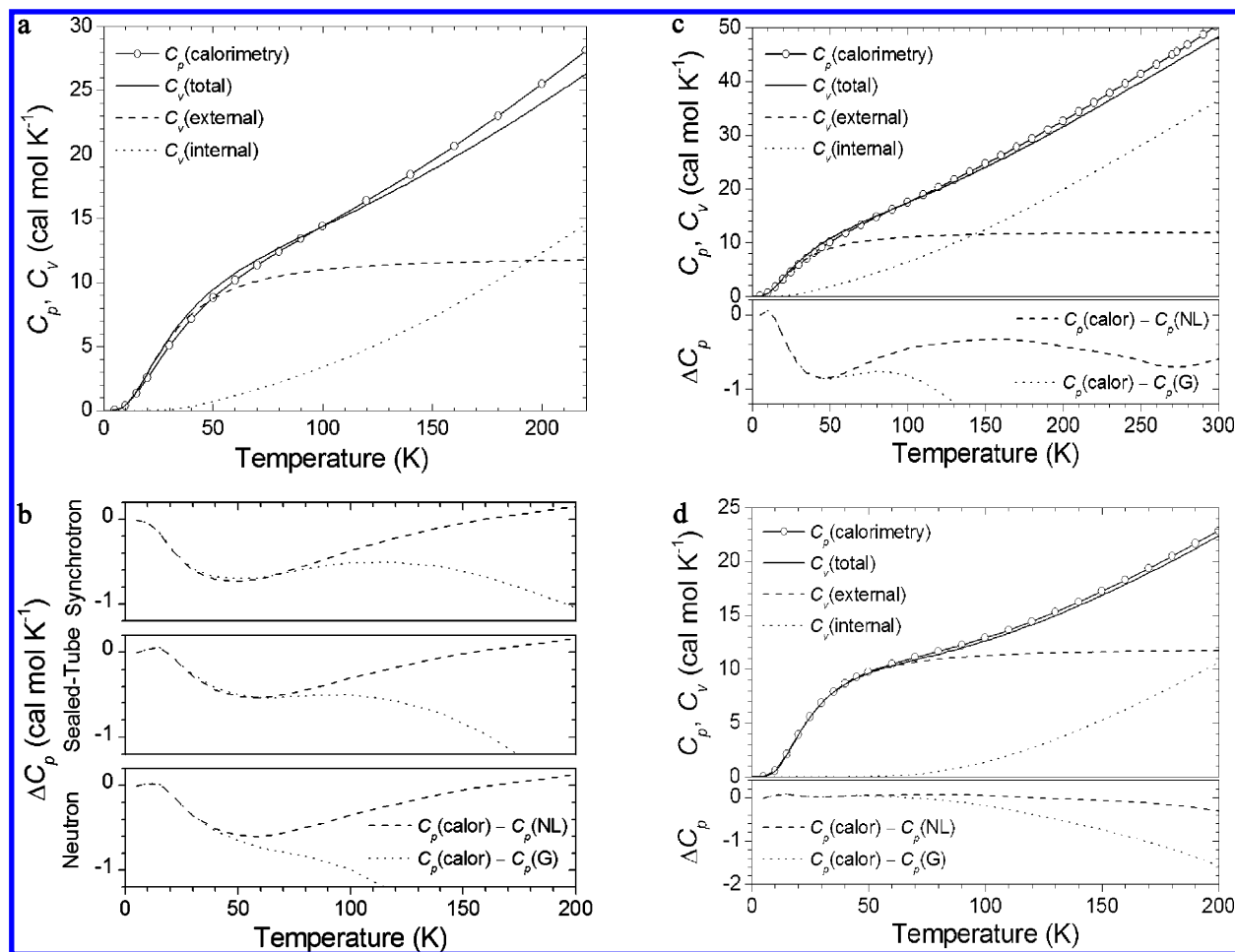
**5.1. Comparison between  $C_p$  Values from ADPs and Calorimetry.** From the models described in section 2 and the frequencies and Grüneisen constants in section 3,  $C_p$  has been calculated and compared to the independent calorimetric measurements, Figure 2a–d. For naphthalene the difference between calorimetry and diffraction experiments is smallest for the combined Debye–Einstein, Nernst–Lindemann approach as may be concluded from the information given in Figures 1a (lower part) and 2a,b (see also the Supporting Information). The effects of the differences in  $C_p$  on the corresponding difference in enthalpies,  $\Delta H(T)$ , and entropies,  $T\Delta S(T)$ , have been calculated at the highest temperature covered by the ADPs. They are the following, in  $\text{cal mol}^{-1}$ : 32.10, 121.46 (1.15%, 2.18%, 0–200 K) for naphthalene sealed-tube X-ray data; 47.21, 182.80 (1.41%, 2.69%, 0–220 K) for naphthalene synchrotron data; 294.86,  $1.23 \times 10^3$  (4.91%, 10.03%, 0–300 K) for naphthalene neutron data;  $-175.90$ ,  $-732.41$  (–2.28%, –4.75%, 0–300 K) for anthracene data; and  $-60.09$ ,  $-227.33$  (–2.34%, –4.15%, 0–200 K) for HMT data. Note the partial compensation of errors in the free energy difference  $\Delta \Delta G(T) = \Delta \Delta H(T) - T\Delta \Delta S(T)$ .

**5.2. Adjustable Parameters.** The calculation of  $C_p(T)$  from ADPs makes use of three parameters: the numerical factor relating  $\nu_E$  to  $\nu_D$  (eqs 5 and 6), the quantity  $A_0$  in the Nernst–Lindemann relation (eq 11), and the scale  $S$  relating ab initio and observed vibrational frequencies (eq 12). In the work presented here none of the three quantities has been adjusted to match  $C_p$  from diffraction experiments to  $C_p$  from calorimetry. For more accurate thermodynamical calculations it may be desirable to consider calculated frequencies corrected for anharmonicity<sup>32,33</sup> and compressibilities measured by variable-pressure powder-diffraction experiments.

**5.3. Comparison between Compressibilities.** The compressibilities have been calculated in the temperature range from 120 K to the maximum experimental temperature and compared with the experimental values at 298 K of naphthalene,<sup>34,35</sup> anthracene,<sup>34–36</sup> and HMT<sup>37,38</sup> (Table 2). Compressibilities estimated from differences between  $C_p$  and  $C_v$  tend to be similar, particularly at 120 K (Table 2, last two columns). They are 2–5 times higher than those obtained from compression experiments and from Grüneisen constants, the latter two being similar. Note that for the naphthalene neutron and anthracene X-ray data, where our estimates exceed this range, the deviations of the ADP-derived data from the calorimetric data in the high-temperature regime are correspondingly large (Figure 2b,c). The origin of the discrepancies in compressibilities is not clear, but could be due to inaccurate estimates of the Grüneisen constant from ADPs or from failure of  $A_0$  to equal the average value reported in the literature.<sup>12</sup> A negatively correlated error in  $\gamma_G$  or  $A_0$  and the frequency scaling factor  $S$  would lead to some compensation of errors in  $C_p$  (eqs 10 and 11).

## 6. Conclusions

ADPs from multitemperature diffraction data provide mean-field frequencies for molecular translations and librations of both the Debye- and Einstein-type. Combined with properly scaled molecular deformation frequencies calculated ab initio, e.g., by DFT-methods, the specific heat of molecular crystals has been derived for naphthalene, anthracene, and HMT. Specific heat curves  $C_p(T)$  from ADPs and calorimetry show better agreement in the low-temperature regime (<120 K) if Debye rather than Einstein frequencies are used for the three translational vibrations. At higher temperatures (>120 K)  $C_p$  calculated from  $C_v$  with the Nernst–Lindemann relation agrees quite well with the



**Figure 2.** Molar heat capacities of (a, b) naphthalene, (c) anthracene, and (d) HMT: calorimetric  $C_p$  (solid line with open circles),  $C_v$  from external vibrations (dashed line),  $C_v$  from internal vibrations (dotted line), and sum of the two (solid line). Differences between  $C_p$  from calorimetry and from the Nernst–Lindemann relation (NL, dashed line) or Grüneisen constant (G, dotted line) are also shown.

**TABLE 2: Comparison of Experimental and Calculated Compressibilities from (1) Grüneisen Constant (eq 9), (2) Difference  $C_p(\text{NL}) - C_v(\text{total})$ , and (3) Difference  $C_p(\text{calor}) - C_v(\text{total})$**

| compd                    | exptl <sup>a</sup> | compressibility ( $10^4 \text{ MPa}^{-1}$ ) obtained from: |  |   |
|--------------------------|--------------------|--|--|---|
|                          |                    | Grüneisen constant   | $C_p(\text{NL}) - C_v(\text{total})^d$ | $C_p(\text{calor}) - C_v(\text{total})^e$ |
| naphthalene <sup>c</sup> | 1.52               | 1.76, –, 1.67 <sup>b</sup>                                 | 3.07, –, 4.05 <sup>b</sup>             | 4.62, –, 3.60 <sup>b</sup>                |
|                          |                    | 2.55, –, 1.99 <sup>b</sup>                                 | 3.90, 4.32 [165], 3.81 <sup>b</sup>    | 6.76, –, 3.34 <sup>b</sup>                |
|                          |                    | 1.55, –, 0.87 <sup>b</sup>                                 | 4.60, 5.23 [170], 3.08 <sup>b</sup>    | 7.91, –, 2.30 <sup>b</sup>                |
| anthracene               | 1.42               | 1.32, –, 0.84 <sup>b</sup>                                 | 3.11, 3.71 [190], 2.93 <sup>b</sup>    | > 16.78, –, 3.69 <sup>b</sup>             |
| HMT                      | 1.15               | 2.05, –, 1.49 <sup>b</sup>                                 | 4.74, 4.86 [135], 3.91 <sup>b</sup>    | 4.73, –, 6.42 <sup>b</sup>                |

<sup>a</sup> Observed compressibility at 298 K: naphthalene,<sup>34,35</sup> anthracene,<sup>34–36</sup> and HMT.<sup>37,38</sup> <sup>b</sup> Continuously decreasing or increasing, calculated compressibilities, which are given at both ends of the temperature ranges: 120–200 (naphthalene sealed-tube data), 120–220 K (naphthalene synchrotron data), 120–300 (naphthalene neutron data), 120–300 (anthracene), and 120–200 K (HMT). If a maximum occurs, it is specified with the corresponding temperature in square brackets. <sup>c</sup> The three data sets for naphthalene are from sealed-tube X-ray,<sup>13</sup> synchrotron,<sup>8</sup> and neutron<sup>8</sup> experiments, respectively. <sup>d</sup> NL denotes Nernst–Lindemann. <sup>e</sup>  $C_v(\text{total})$  is the sum of contributions from external and internal vibrations.

calorimetric data for all compounds investigated here. The approach described in this work can be applied to study solid–solid-phase transitions in polymorphic compounds provided both phases can be studied over a sufficiently large temperature range including very low temperatures. This is always possible when the stable high-temperature structure, which is metastable at low temperature, can be quenched.

In the absence of reliable calorimetric measurements and given the fact that experimental programs aimed at measuring thermodynamic quantities appear more difficult to fund than diffraction measurements,  $C_v$  and  $C_p$  for molecular crystals calculated from atomic displacement parameters covering a large enough temperature range are a reasonable alternative to calorimetric data. Compressibility values at room temperature

obtained experimentally over 50 years ago with the Bridgman compressibility apparatus<sup>39</sup> and confirmed more recently<sup>34,38</sup> are smaller than the estimates given here by factors of about two to five. As high-pressure diffraction facilities become increasingly available,<sup>40–43</sup> it also will become possible to determine compressibility as a function of temperature,  $\kappa(T)$ , and thus to achieve a better understanding of  $C_v(T)$  determined from atomic displacement parameters.

**Acknowledgment.** We thank Dr. S. C. Capelli for communicating her results prior to publication and the Swiss National Science Foundation for financial support.

**Supporting Information Available:** Volume expansion, external frequencies, and Eigenvectors from normal coordinate

analysis of multitemperature ADPs for anthracene and HMT; frequencies of internal vibrations from DFT calculations and spectroscopy for naphthalene, anthracene, and HMT; and heat capacity estimated with the Einstein, Debye, and Nernst–Lindemann models for naphthalene sealed-tube X-ray, neutron data, and anthracene data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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