

## Possible Dimensional Effect on the Heat Capacity of Molecular Solids

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A contribution to the heat capacity that is linear in  $T$  has been measured for solid argon and for two solid isotopic methanes in the region  $0.25 < T < 4$  K. The effect is observed because of exceptional circumstances where a small specimen is contained in a relatively large calorimeter vessel. It is suggested that the same effect may account for some unexplained observations on solid  $^3\text{He}$  and solid  $^4\text{He}$ .

In connection with a study of the thermodynamic properties of solid isotopic methanes in the region  $T < 4$  K, we have encountered an unexpected contribution to the heat capacity that is linearly dependent upon the temperature. Its magnitude is inversely proportional to the specimen thickness (or the surface density) over the range of sizes of specimen that could be investigated practically with our calorimetric apparatus. The linear temperature dependence of the heat capacity seems to rule out the possibility that the effect is caused by the specimens being in the form of small particles in the calorimeter vessel. Surface or particle-size effects lead<sup>1</sup> to a temperature dependence of the surface heat capacity of the approximate form  $C_s \propto T^{2.5}$  in the region  $T < 0.5\theta$ , where  $\theta$  is an average characteristic temperature of the lattice. Moreover, the average thickness of our specimens ( $\sim 10^5$  Å) was two or three orders of magnitude larger than particle sizes that would be expected to yield a measurable effect on the bulk heat capacity.

Our investigation began with the observation of a troubling systematic difference between our measurements<sup>2,3</sup> of the heat capacities of solid  $\text{CH}_3\text{D}$  and  $\text{CH}_2\text{D}_2$  and some earlier results<sup>4,5</sup> for the region  $1 < T < 4$  K. The difference was several times larger than the combined probable uncertainties in the different calorimetric experiments. Obvious possible systematic errors in the temperature scale, the measurement of the amounts of the specimens, the thermal treatment of the specimens, and the determination of the heat capacity of the empty calorimeter were sought through carefully conducted check experiments and none were found. Finally, in order to eliminate any possible subtle effects caused by the complex behavior of solid methanes at low temperatures, experiments were performed with argon in the calorimeter vessel in amounts comparable to those of the calorimetric specimens of the methanes. The results correlate well with those for the methanes. Further investigation ex-

tends the correlation to include linear temperature contributions to the heat capacities of solid  $^3\text{He}$  and  $^4\text{He}$  that have been observed<sup>6</sup> but not explained.<sup>7</sup>

For the new experiments<sup>2,3</sup> on  $\text{CH}_3\text{D}$  and  $\text{CH}_2\text{D}_2$ , isotopically purified materials were used but they were available only in small amounts ( $\leq 100$  cm<sup>3</sup> at STP). Each specimen was sealed in turn in a light-weight calorimeter vessel (volume  $\sim 120$  cm<sup>3</sup>; surface area  $\sim 156$  cm<sup>2</sup>) which carried a calibrated germanium thermometer and a heater and which was mounted below the mixing chamber in a helium dilution refrigerator. This style of calorimeter was chosen so as to eliminate filling tubes that always complicate calorimetry at very low temperatures.

Since it takes a few hours to cool the dilution refrigerator from 80 K to liquid-helium temperatures, it is very improbable that the solid specimens in the calorimeter vessel were strained in any significant way. Experiments were performed in which the  $\text{CH}_2\text{D}_2$  specimen was annealed for many hours at temperatures above 50 K but that thermal treatment produced no detectable change in the heat capacity of the solid at low temperatures. The physical state of the solid inside the vessel is not known for certain, of course, but it seems most probable that the solid was distributed more or less uniformly over the inside surface. Anything different from that could only have been produced by a steep temperature gradient in the cryostat during the cooling. The cryostat has two inner cylindrical cans made of thick copper which militate against a steep gradient being developed.

The results of the experiments are displayed in Fig. 1. For clarity, the experimental points are plotted only for the argon specimens. The error bars include the consequence of the specimens contributing only (20–25)% of the total heat capacity of the calorimeter system. The points represent the molar heat capacity in excess of the heat capacity of bulk argon, which is known to high ac-

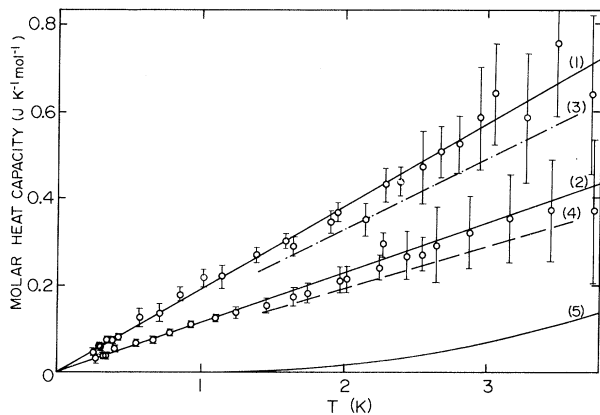


FIG. 1. Molar excess heat capacities as a function of temperature. Curve (1), argon I,  $2.10 \times 10^{-3}$  moles; curve (2), argon II,  $3.52 \times 10^{-3}$  moles; curve (3),  $\text{CH}_2\text{D}_2$ ,  $2.59 \times 10^{-3}$  moles; curve (4),  $\text{CH}_3\text{D}$ ,  $4.45 \times 10^{-3}$  moles. [For reference, curve (5), heat capacity of bulk argon (Ref. 8).]

curacy.<sup>8</sup> The large relative magnitude of the linear contribution can be judged with reference to curve (5) which represents the bulk heat capacity. The straight lines (1) and (2) represent least-squares fits to the excess heat capacities of the argon specimens. The dash-dotted (3) and dashed (4) lines depict the systematic differences in the heat capacities of  $\text{CH}_3\text{D}$  and  $\text{CH}_2\text{D}_2$  that initiated the investigation.

The coefficients of the linear temperature contributions to the heat capacity (the slopes of the lines in Fig. 1) are given under *A* in the second column of Table I together with, under *B*, the surface density of the specimens expressed in moles per square centimeter. The product  $A \times B$ , given in the last column, is a constant within an average deviation of 4%. Thus, the effect,  $\Delta C$

$= AT$ , clearly depends upon the average thickness of the specimen and is not specific to the substance, although it should be noted that solid argon and the solid methanes have similar Debye characteristic temperatures.

In the lower part of Table I, similar data obtained by Castles and Adams<sup>6</sup> from heat capacities of solid  $^3\text{He}$  and solid  $^4\text{He}$  are listed. The contributions to the heat capacity that they found to be linear in  $T$  have not been explained and they were not reproduced in a recent comprehensive study by Greywall.<sup>7</sup> Indeed, Greywall examined all of the conceivable sources of systematic or other experimental error in the different experiments and was not able to find one that could produce a contribution to the heat capacity of the solid of the form  $\Delta C = AT$ .

As we see in Table I, the product  $A \times B$  from the helium experiments is within a factor of 7 or less of the values for the argon and methane specimens. This strongly suggests that the observed linear contributions to the heat capacity have a common origin. Also, it should be pointed out that the conditions of Greywall's experiments were such that he would not have been able to observe the effect. In particular, if we take  $A \times B = 1 \times 10^{-6} \text{ J/deg}^2 \text{ cm}^2$  as an average value for that product, *A* for Greywall's experiments would only have been about 1% of the electronic contribution to the heat capacity of his calorimeter vessel.

We will not speculate here as to the origin of the effect that we have characterized. Unexpected linear contributions to the heat capacities of glasses at very low temperatures have been observed<sup>9</sup> and several different explanations<sup>10-12</sup> have been advanced for the observations. It is by no means obvious that any of them can be adapted to account for the results reported here.

TABLE I. Correlation of linear contribution to the heat capacity with surface density.

	<i>A</i> slope (J/mole deg <sup>2</sup> )	<i>B</i> surface density (mole/cm <sup>2</sup> )	<i>A</i> × <i>B</i> (J/deg <sup>2</sup> cm <sup>2</sup> )
Argon I	0.191	$1.34 \times 10^{-5}$	$2.57 \times 10^{-6}$
Argon II	0.108	$2.26 \times 10^{-5}$	$2.44 \times 10^{-6}$
$\text{CH}_2\text{D}_2$	0.163	$1.66 \times 10^{-5}$	$2.71 \times 10^{-6}$
$\text{CH}_3\text{D}$	0.098	$2.84 \times 10^{-5}$	$2.78 \times 10^{-6}$
Castles and Adams <sup>a</sup>			
$^3\text{He}(24.40 \text{ cm}^3/\text{mole})$	0.0095	$1.35 \times 10^{-4}$	$1.29 \times 10^{-6}$
$^3\text{He}(21.67 \text{ cm}^3/\text{mole})$	0.0055	$1.52 \times 10^{-4}$	$8.3 \times 10^{-7}$
$^4\text{He}(20.59 \text{ cm}^3/\text{mole})$	0.0025	$1.59 \times 10^{-4}$	$4.0 \times 10^{-7}$

<sup>a</sup>Ref. 6.

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## Critical Suppression of Birefringence in a Smectic-A Liquid Crystal near the Smectic-C Phase

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An unusual minimum in the optical birefringence has been observed at the smectic-A to smectic-C transition temperature of 4-*n*-pentylphenylthiol-4-*n'*-octyloxybenzoate. The results are interpreted in terms of the reduction of the birefringence by short-range smectic-C order in the smectic-A phase. Data analysis yields a specific-heat critical exponent  $\alpha$  of  $0.32 \pm 0.12$ .

The smectic-A to smectic-C (AC) phase transition in liquid crystals is generally believed to be second order. Various critical phenomena have been predicted by de Gennes.<sup>1</sup> The heliumlike order parameter  $\psi$  is taken to be  $\theta \exp(i\varphi)$ , where  $\theta$  is the tilt and  $\varphi$  the azimuthal angle of the molecules. Measurements have been made of the pretransitional behavior of the order parameter<sup>2-6</sup> and the susceptibility.<sup>7,8</sup> The values of the critical exponents reported are not heliumlike.

We report in this Letter the first measurement in detail of the optical birefringence  $\Delta n$  near the AC transition. Studies of  $\Delta n$  near transitions involving smectic phases are potentially useful because of the coupling between the orientational order and the smectic orders. Near a nematic-smectic-A (NA) transition, the occurrence of long-range layerlike order favors stronger orientational order and results in an increase in  $\Delta n$  on the smectic-A side.<sup>1,9</sup> On the nematic side, short-range translational order should also enhance  $\Delta n$ . Such a pretransitional enhancement has been observed.<sup>10</sup> Near an AC transition, however, the effect of the critical behavior on  $\Delta n$  might be quite different. Fluctuations in  $\psi$ , being angular in nature, are disruptive to the orienta-

tional order. It is therefore conceivable for short-range smectic-C order to result in a measurable *suppression* of  $\Delta n$  in the smectic-A phase. We have observed this pretransitional reduction in  $\Delta n$ . The data have also enabled us to obtain a value for the specific-heat critical exponent  $\alpha$ .

Planar samples between glass slides are studied, with the smectic layers normal to the slides as shown in Fig. 1. A rotating-analyzer technique

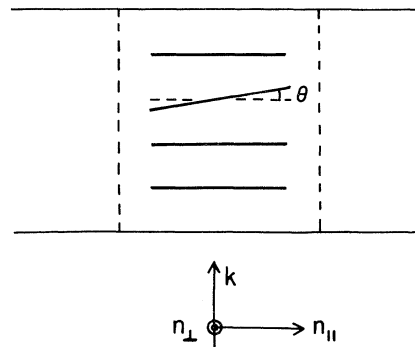


FIG. 1. Planar sample geometry for measuring birefringence  $\Delta n = n_{\parallel} - n_{\perp}$  with light incident along  $\vec{k}$ . The heavy lines represent local directors.