[4] J. Sakurai, R. A. Cowley, and G. Dolling, J. Phys. Soc. Jpn. 28, 1426 (1970).

[5] V. Heine and J. D. C. McConnell, Phys. Rev. Lett. 46, 1092 (1981).

[6] A. Pullman and H. Berthod, Chem. Phys. Lett. 81, 195 (1981).

[7] W. Marshall and S. W. Lovesey, *Theory of Thermal Neutron Scattering* (Clarendon, Oxford, 1971).

[8] J. M. Rowe, J. J. Rush, N. J. Chesser, K. H. Michel, and J. Naudts, Phys. Rev. Lett. 40, 455 (1978).

Approach to Melting in Ammonia as a Critical Transition

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The molar volumes of ammonia solid I and solid II were measured from 0.5 to 14.0 kbar and 185 to 320 K. Over regions that extend 3 kbar and 20 K into the solid phases, variations in compressibility and thermal expansion can be described by power laws with exponents similar to those usually associated with critical transitions. It is suggested that breaking of hydrogen bonds may account for the extreme softening of solid ammonia.

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Just before melting, many elements and compounds exhibit unusual behavior[1] marked by large increases in the isothermal compressibility,[2] $\kappa_T \equiv -V^{-1}(\partial V/\partial p)_T$, and in the isobaric thermal expansion,[3-5] $\alpha_p \equiv V^{-1}(\partial V/\partial T)_p$; large decreases in the frequency of low-lying phonon-libron modes[6]; and the vanishing of certain elastic constants.[7-8] These abnormal effects lead *a priori* to various kinds of instability in the solid.[9] We report here volumetric measurements that show that solid ammonia undergoes a dramatic softening on approach to melting. In the homogeneous solid phase, κ_T and α_p follow power laws indicative of a λ-type transition. We suggest that the wide range in p and T over which this behavior is observed makes ammonia an ideal subject for study of the anomalous effects that precede melting. Detailed knowledge about solid NH_3 is also needed to interpret data relating to planetary atmospheres.[10]

We used a piston-cylinder apparatus, designed for condensed gases,[11] to measure the p-V-T properties of 99.99% pure ammonia from about 185 to 320 K and 0.5 to 14.0 kbar. The phase diagram of condensed NH_3, along with experimental details, are given elsewhere.[12] Briefly, we found that the melting curve has two branches, as implied by the work of Vereshchagin and Voronov[13] and Hanson and Jordan.[14] The lower branch, bounding solid I, is given by

$$p_m(\mathrm{I}) = 5.886\,[(T_m/T_{g\text{-}l\text{-}\mathrm{I}})^{3.960} - 1], \tag{1a}$$

and the upper one, bounding solid II, is given by

$$p_m(\mathrm{II}) = 11.156\,[(T_m/T_{l\text{-}\mathrm{I}\text{-}\mathrm{II}})^{1.516} - 1] + 3.070, \tag{1b}$$

where $p_m(\mathrm{I,II})$ is the melting pressure in kilobars, T_m is the melting temperature in kelvins, $T_{g\text{-}l\text{-}\mathrm{I}} = 195.48$ K is the gas-liquid-solid I triple-point temperature,[15] and $T_{l\text{-}\mathrm{I}\text{-}\mathrm{II}} = 217.34$ K is the liquid-solid I-solid II triple-point temperature. The two curves intersect at $p_m(\mathrm{I,II}) = 3.070$ kbar, from which point a solid I-solid II transition line rises steeply in the p-T plane. We assume that ammonia solid I has a simple-cubic structure similar to that found in x-ray[16] and neutron-diffraction[17] studies made more than 20 K below $T_{g\text{-}l\text{-}\mathrm{I}}$ at 1 bar. Solid II is thought to be face-centered cubic from preliminary x-ray measurements carried out in a diamond cell at room temperature.[18]

The molar volume of solid I was measured along five isotherms and three isobars to a distance of about 3 kbar and 20 K, respectively, from the melting curve, giving a total of 140 data points. For solid II we obtained 460 points along fourteen isotherms and seven isobars out to about the same distance from the melting line.

Several typical isotherms are shown in Fig. 1, where the upper experimental points represent liquid volumes V_l and the lower points represent solid-II volumes $V_s(\mathrm{II})$. As the melting curve is approached from the solid side, $V_s(\mathrm{II})$ undergoes a progressive enhancement that begins more than

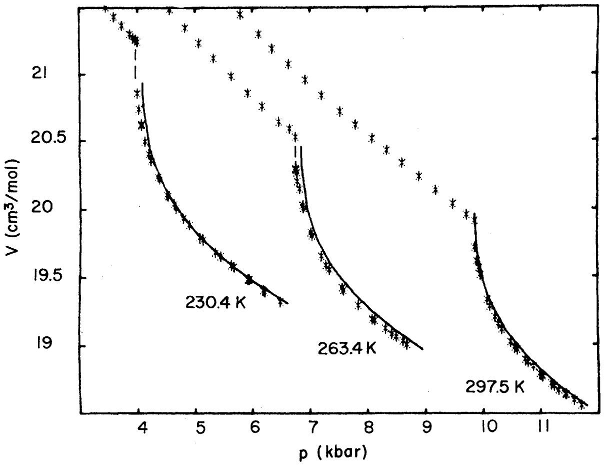

FIG. 1. Molar volume of ammonia as a function of pressure along isotherms at 230.4, 263.4, and 297.5 K. Upper branches, liquid; lower branches, solid II; solid lines, EOS Eq. (3) with Eqs. (1b) and (4b); dashed lines, volume change on melting.

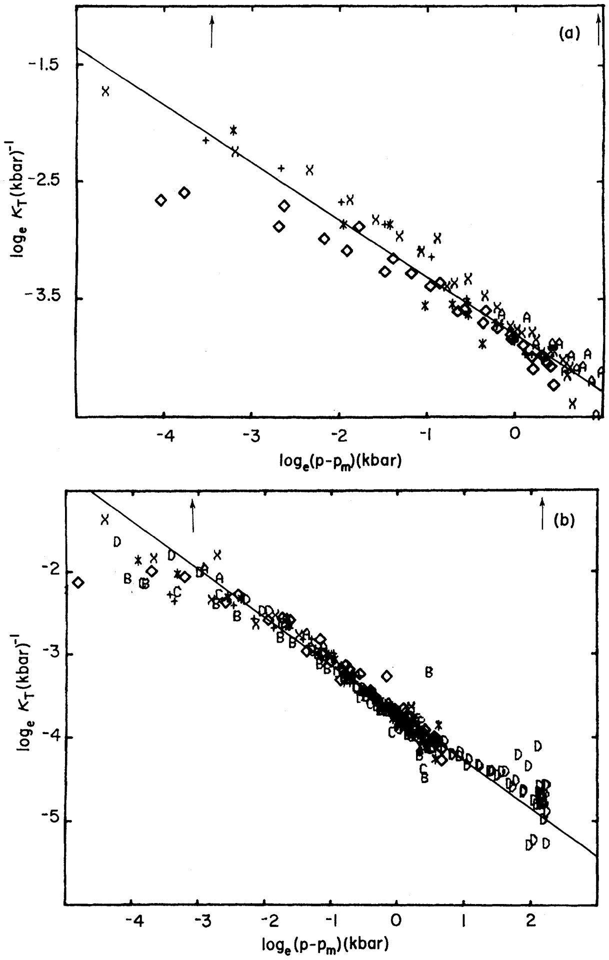

FIG. 2. $\ln\kappa_T$ as a function of $\ln(p-p_m)$ along isotherms in solid ammonia. Arrows show regions of linear variation. Friction in the piston caused reduced accuracy in points taken below about $p-p_m = 50$ bar. (a) Solid I. A's, 192.5 K; crosses, 202.0 K; asterisks, 206.9 K; diamonds, 214.5 K; plusses, 215.2 K. (b) Solid II. Diamonds, 222.4 K; D's, 230.4 K; crosses, 244.0 K; A's, 254.6 K; asterisks, 263.5 K; B's, 274.0 K; plusses, 282.8 K; C's, 297.5 K.

2 kbar from p_m and is finally interrupted by the discontinuous volume change on melting $\Delta V_m = V_{l,m} - V_{s,m}(\mathrm{II})$. We observed similar behavior in the solid-I molar volume $V_s(\mathrm{I})$ and also in plots of $V_s(\mathrm{I})$ and $V_s(\mathrm{II})$ along isobars, beginning at a distance $T_m - T = 20$ K from melting. Over this range κ_T and α_p, computed from the data, increased by one order of magnitude.

As shown in Fig. 2, plots of $\ln\kappa_T$ vs $\ln(p-p_m)$ are linear and independent of T for both solids, leading to the analytical expression

$$\kappa_T = k(p-p_m)^{-\gamma}, \tag{2}$$

where k and γ are constants. A least-squares fit gives $\gamma = 0.49$ for solid I and $\gamma = 0.60$ for solid II. By integrating Eq. (2) along isothermal paths one gets

$$V_s = V_c \exp[-k(1-\gamma)^{-1}(p-p_m)^{1-\gamma}], \tag{3}$$

where p_m is given by Eqs. (1a) and (1b) and V_c is the value of the solid volume V_s when $p = p_m$. For all of the solid isotherms, Eq. (3) provided excellent fits in which k remained quite constant and V_c was found to be in the range $V_{s,m} < V_c < V_{l,m}$.

Complete equations of state (EOS) for ammonia solids I and II were derived by expressing V_c in Eq. (3) as a function of temperature. We found that V_c could be fitted with acceptable accuracy by

$$V_c(\mathrm{I}) = V_{\mathrm{I}} - d_{\mathrm{I}}(T - T_{g\text{-}l\text{-}\mathrm{I}}) \tag{4a}$$

for solid I, and by

$$V_c(\mathrm{II}) = V_{\mathrm{II}} - d_{\mathrm{II}}(T - T_{l\text{-}\mathrm{I}\text{-}\mathrm{II}}) \tag{4b}$$

for solid II, where $V_{\mathrm{I,II}}$ and $d_{\mathrm{I,II}}$ are constants and the triple-point temperatures are those used in Eqs. (1a) and (1b). Values of the parameters in Eqs. (2), (3), (4a), and (4b) for solids I and II are presented in Table I. After substituting Eqs. (1a), (1b), (4a), and (4b) into Eq. (3), we were able to fit all of the isothermal V_s data by the EOS with an average relative error in V_s of 4×10^{-3} and a maximum relative error of 10^{-2}. The incorporation of isobaric data in the fit

TABLE I. Values of the parameters in Eqs. (2)–(6), derived[a] from isothermal data for ammonia solid I and solid II.

Solid	γ	$k\gamma^{-1}$ (kbar)	V (cm^3/mol)	d (cm^3/mol K)
I	0.49 ± 0.02	0.0281 ± 0.0006	21.61 ± 0.03	0.0316 ± 0.0010
II	0.60 ± 0.01	0.0225 ± 0.0003	21.13 ± 0.02	0.0146 ± 0.0002

[a] γ was determined from plots of $\ln\kappa_T$ vs $\ln(p - p_m)$; k, V, and d were evaluated from fits of all the p-V-T data using Eq. (3) with Eqs. (1a), (1b), (4a), and (4b).

raised[19] the average error to 7×10^{-3}. Within the accuracies mentioned above, the EOS can be used for solids I and II up to 3 kbar above p_m or about 20 K below T_m.

From Eq. (3) one can obtain the expression

$$\alpha_p = \kappa_T\, dp_m/dT_m + V_c^{-1} dV_c/dT. \tag{5}$$

Equation (5), derived earlier by Buckingham and Fairbank[20] for the λ transition in liquid ^{4}He, shows that the ratio α_p/κ_T remains finite and assumes the asymptotic limit dp_m/dT_m as the critical point is approached. This asymptotic behavior, which seems to be a feature of continuous transitions where α_p and κ_T diverge,[5] was first pointed out by Pippard[21] and recently derived by Soulard.[22] We show the behavior of ammonia solid II along several isochors in Fig. 3, where the points are derived from the EOS Eq. (3) and the melting curve is from Eq. (1b).

Starting with Eq. (5) and using Eqs. (1a) and (1b), one can also arrive at an equation for α_p in terms of $(T_m - T)$. The result is

$$\alpha_p = k(T_m - T)^{-\gamma}(dp_m/dT_m)^{1-\gamma}, \tag{6}$$

which reproduces the measured values of α_p within experimental uncertainty.[19]

We have shown that the approach to melting in solid ammonia can be described in terms of a critical phenomenon wherein the solid exhibits values of κ_T and α_p that are 10 times larger than those of the liquid at melting. In this state there are sizable fluctuations in density and entropy that can cause instability and, eventually, melting. It is interesting to note that V_c for ammonia is always larger than $V_{s,m}$. Furthermore, when the isotherms were fitted by the three parameters V_c, k, and a critical pressure p_c rather than p_m, p_c was generally found to be a few tens of bars smaller than p_m. This indication of a critical state lying below the melting curve agrees with experimental and theoretical conclusions about shear instability and melting in alkali halides.[7,9,23]

The microscopic mechanism that leads to anomalous melting in ammonia may be related to orientational motion of NH_3 molecules on the solid-I and solid-II lattices. Diffraction studies[16,17] made on solid I at 77 and 171 K show that each hydrogen atom, in addition to its H-N intramolecular covalent bond of 1.005 Å, also has an intermolecular hydrogen bond of 2.374 Å to the nitrogen in an adjoining NH_3 molecule. Thus each nitrogen is hydrogen bonded to six neighboring nitrogen atoms. The progressive breaking of these weak bonds could lead to reorientation of molecules, softening of crystal modes, instability, and melting. In our ammonia p-V-T study, described more completely elsewhere,[12] we measured also the speed of 10- and 30-MHz sound. We found essentially complete attenuation of the signal in the solid-I and -II regions extending 20 K below melting, which suggests that there are mechanisms coupling these ultrasonic frequencies with phonon and libron modes in the crystal. Heat-capacity

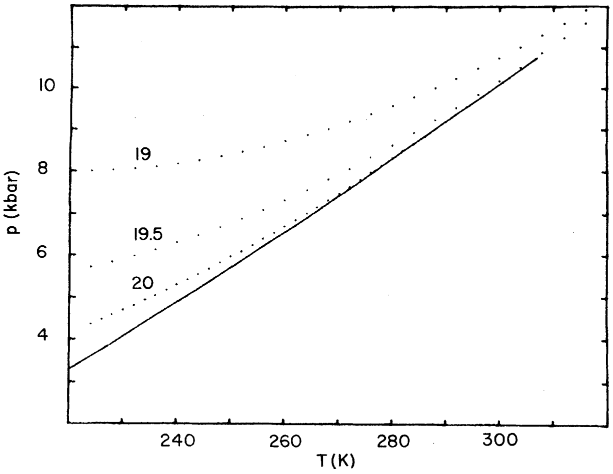

FIG. 3. Ammonia solid-II isochors at 19.0, 19.5, and 20.0 cm^3/mol in the p-T plane. Points, derived from Eq. (3); solid line, Eq. (1b).

measurements[24] made at 1 bar on solid I also show a progressive departure from Debye behavior over the last 20 K on approach to melting.

The exponent γ in Eq. (2) has a different value in solid I from that in solid II, which could result from differences in the two crystal structures. Nevertheless it seems likely that hydrogen bonding occurs in solid II as well as in solid I. Both γ exponents are near the value 0.5 calculated by Boyer[9,23] for α_p in alkali halides, using a model based on quasiharmonic theory.

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[1] A. R. Ubbelohde, *The Molten State of Matter (Melting and Crystal Structure)* (Wiley, New York, 1978).

[2] P. Figuiere, A. H. Fuchs, M. Ghelfenstein, and H. Szwarc, J. Phys. Chem. Solids 39, 19 (1978).

[3] L. Ter Minassian and Ph. Pruzan, J. Chem. Thermodyn. 9, 375 (1977).

[4] A. H. Fuchs, Ph. Pruzan, and L. Ter Minassian, J. Phys. Chem. Solids 40, 369 (1979).

[5] Ph. Pruzan, L. Ter Minassian, and A. Soulard, in *High-Pressure Science and Technology,* edited by K. D. Timmerhaus and M. S. Barber (Plenum, New York, 1979), Vol. 1, p. 368.

[6] M. Chelfenstein and H. Szwarc, Chem. Phys. Lett. 32, 93 (1975).

[7] O. D. Slagle and H. A. McKinstry, J. Appl. Phys. 38, 437 (1967).

[8] I. N. S. Jackson and B. C. Liebermann, J. Phys. Chem. Solids 35, 1115 (1974).

[9] L. L. Boyer, in *Thermal Expansion 7,* edited by D. C. Larsen (Plenum, New York, to be published).

[10] L. S. Slobodkin, I. F. Barykov, R. D. Cess, and J. Caldwell, J. Quant. Spectrosc. Radiat. Transfer 20, 481 (1978).

[11] R. L. Mills, D. H. Liebenberg, and J. C. Bronson, Phys. Rev. B 21, 5137 (1980).

[12] R. L. Mills, D. H. Liebenberg, and Ph. Pruzan, to be published.

[13] L. F. Vereshchagin and F. F. Voronov, Zh. Fiz. Khim. 30, 329 (1956).

[14] R. C. Hanson and M. Jordan, J. Phys. Chem. 84, 1173 (1980).

[15] L. Haar and J. S. Gallagher, J. Phys. Chem. Ref. Data 7, 635 (1978).

[16] I. Olovsson and D. H. Templeton, Acta Crystallogr. 12, 832 (1958).

[17] J. W. Reed and P. M. Harris, J. Chem. Phys. 35, 1730 (1961).

[18] R. C. Hanson, private communication.

[19] The apparatus was designed for isothermal runs. Data taken along isobars are of lower accuracy, which makes an analysis of the variation α_p vs $T_m - T$ less precise.

[20] M. J. Buckingham and W. M. Fairbank, in *Progress in Low Temperature Physics,* edited by C. J. Gorter (North-Holland, Amsterdam, 1961), Vol. 3, Chap. 3.

[21] A. B. Pippard, Philos. Mag. 8, 473 (1956).

[22] A. Soulard, C. R. Acad. Sci. 282, 535 (1976), and 287, 113 (1978).

[23] L. L. Boyer, Phys. Rev. B 23, 3673 (1981).

[24] R. Overstreet and W. F. Giauque, J. Am. Chem. Soc. 59, 254 (1937).