Phase Diagrams to High Pressures of the Univalent Azides Belonging to the Space Group D_{4h}^{18}-$I4/mcm$

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The high-pressure phase diagrams of CsN_3, TlN_3, RbN_3, and KN_3 were studied by means of differential thermal analysis and volume displacement. These substances decompose explosively near $\sim460°C$ even at high pressures. CsN_3, TlN_3, and RbN_3 each have a new high-pressure transformation with a volume change of $\sim3.5\%$ near 6 kbar at 25°C. The transition pressures increase with temperature. In the case of CsN_3 this transition line meets the tetragonal/bcc transition line at a triple point at 173°C, 8 kbar. The resulting CsN_3 III/bcc phase boundary was followed to 37 kbar, where it is terminated by explosive decomposition. The TlN_3 tetragonal/bcc boundary was followed to 20 kbar, where it is also terminated. The melting curves of KN_3 and TlN_3 were followed only to ~5 kbar, where they are terminated.

INTRODUCTION

Ionic crystals which consist of spherical cations and rod-shaped anions usually undergo a phase transition at high temperature. The transition involves a change in the orientation of the anions due to thermal disorder and may be of the first order or very often of a higher order. If the anion is assumed to consist of three atoms, it may be asymmetrical, as in the case of KSCN, or it may be symmetrical, as in the cases of RbN_3 or KHF_2. In addition to the thermal polymorphism to be expected for the second case, substances with asymmetrical anions upon heating usually first undergo a transition to a phase where the anions are oriented in such a way that their asymmetrical character disappears on the average. The transition KSCN II/I at $\sim141°C$[1–3] is an example. The low-temperature phase is orthorhombic, space group D_{2h}^{11}, with the anions arrayed alternately as SCN^- and NCS^-.[4–5] The transition is caused by the dynamical disordering of the direction of anions in the crystal due to the excitation of the out-of-plane torsional oscillation and the flipping motion, so that the anions in the high-temperature phase are randomly arrayed as SCN^- and NCS^-. The high-temperature phase therefore possesses the KHF_2 structure[6] and is tetragonal, space group D_{4h}^{18}-$I4/mcm$.

The azides of potassium, rubidium, cesium, and univalent thallium have the same structure as KHF_2 at room temperature and pressure.[7] This structure is a distorted cesium chloride structure, with the distortion being caused by the symmetrical rod-shaped N_3^- or HF_2^- ions. At sufficiently high temperatures this structure can be expected to transform to the cesium chloride structure due to large thermal disorder of the anions. This transition occurs at 315°C for RbN_3,[7]

151°C for CsN_3,[7] and 295°C for TlN_3.[8] Geometrical and thermodynamic considerations show[7] that free rotation of the anions is not likely to occur, and the observed x-ray intensities for the high-temperature phase are in good agreement with those calculated on the assumption of random orientation of the azide ions parallel to the edges of the cubic unit cell. Whereas in the low-temperature phase the orientation of a particular azide ion is fully determined by the positions of its neighbors, in the high-temperature phase it may be found with almost equal probability parallel to any of the three axes of the cubic unit cell. The transition temperatures increase linearly with decreasing cation radius, and the corresponding transition for KN_3 is therefore not expected to occur before $\sim475°C$, which is well above the melting point.[7]

EXPERIMENTAL

CsN_3 and RbN_3 with a purity of 99.9% were obtained from Electronic Space Products, Inc., and KN_3 with the same purity from K & K Laboratories, Inc. TlN_3 was prepared by precipitation from aqueous solutions of A.R. grade NaN_3 and Tl_2CO_3, and thorough washing with water and ethanol. All salts were carefully dried before use.

Pressures up to 40 kbar were generated in a piston-cylinder device.[9] The furnace assembly was similar to that used by Cohen *et al.*[10] Phase changes were detected by means of differential thermal analysis (DTA) using Chromel–Alumel thermocouples corrected for the effect of pressure.[11] The samples were contained in metal capsules which incorporated thermocouple wells.[12] Most of the work was done using Ag capsules, but results in Al or Cu capsules were in agreement with

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those obtained in Ag capsules. The axial thermal gradient along the sample capsule was reduced by sandwiching the capsule between two insulated metal plugs.[13] Typical DTA signals obtained are shown in Fig. 1. Each phase boundary is based on several separate runs. The results of different runs were consistent within ∼2°C. The heating/cooling rate was in the range 0.2–0.9°C/sec. Sliding friction in the case of solid–solid transitions was determined by comparing results obtained on increasing and on decreasing pressure. The pressures obtained in this way were further corrected for the effect of nonsymmetrical pressure losses. The procedure has been described elsewhere.[14] The azides studied here decompose explosively, even at high pressures, at comparatively low temperatures, and it was never possible to obtain downstroke sliding friction for the melting curves. The observed points were instead corrected by amounts estimated from previous experience in the same pressure–temperature regions. The corrected pressures are believed accurate to ±0.5 kbar for solid–solid transitions and ±1.5 kbar for the melting curves. The points plotted represent the mean of heating and cooling in the case of solid–solid transitions, and melting temperatures in the case of solid–liquid phase changes.
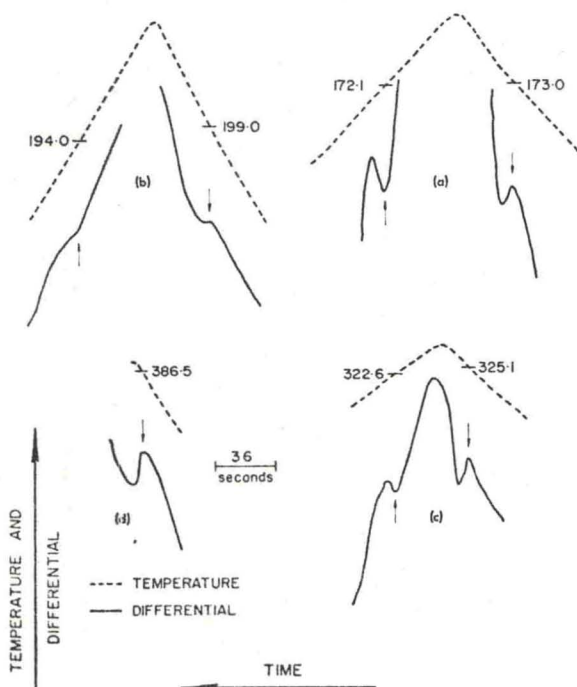

FIG. 1. Typical DTA signals obtained: (a) CsN_3 I/II transition at 7.4 kbar. (b) CsN_3 I/III transition at 9.8¼ kbar. Note the considerable increase in hysteresis and sluggishness as compared to the I/II transition. (c) TlN_3 I/II transition at 3.0 kbar. (d) KN_3 melting at 2.3 kbar. Heating was stopped before the melting was completed, and no freezing signals are therefore seen.
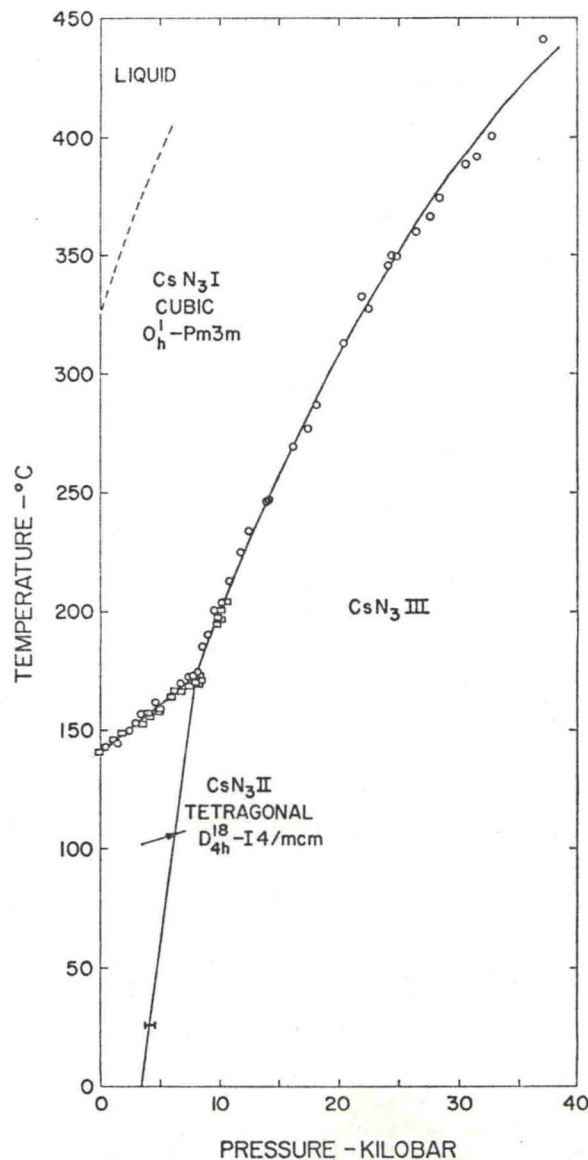

FIG. 2. Phase diagram of CsN_3 to 37 kbar.

Possible high-pressure polymorphism was studied by wrapping 5–10 g of the sample in a thin lead foil and inserting this into the pressure vessel, the walls of which were coated with Molykote to minimize friction. Stoppers of talc were used at the upper end of the bore of the pressure vessel to prevent extrusion of the sample when pressure was applied. After precompression to ≈40 kbar, the displacement of the piston was measured as a function of pressure, using a dial gauge readable to 0.0003 cm. This volume-discontinuity method was further refined by using piston rotation[15] to minimize friction at a transition. The details of the method have been fully described elsewhere.[16] Tem-

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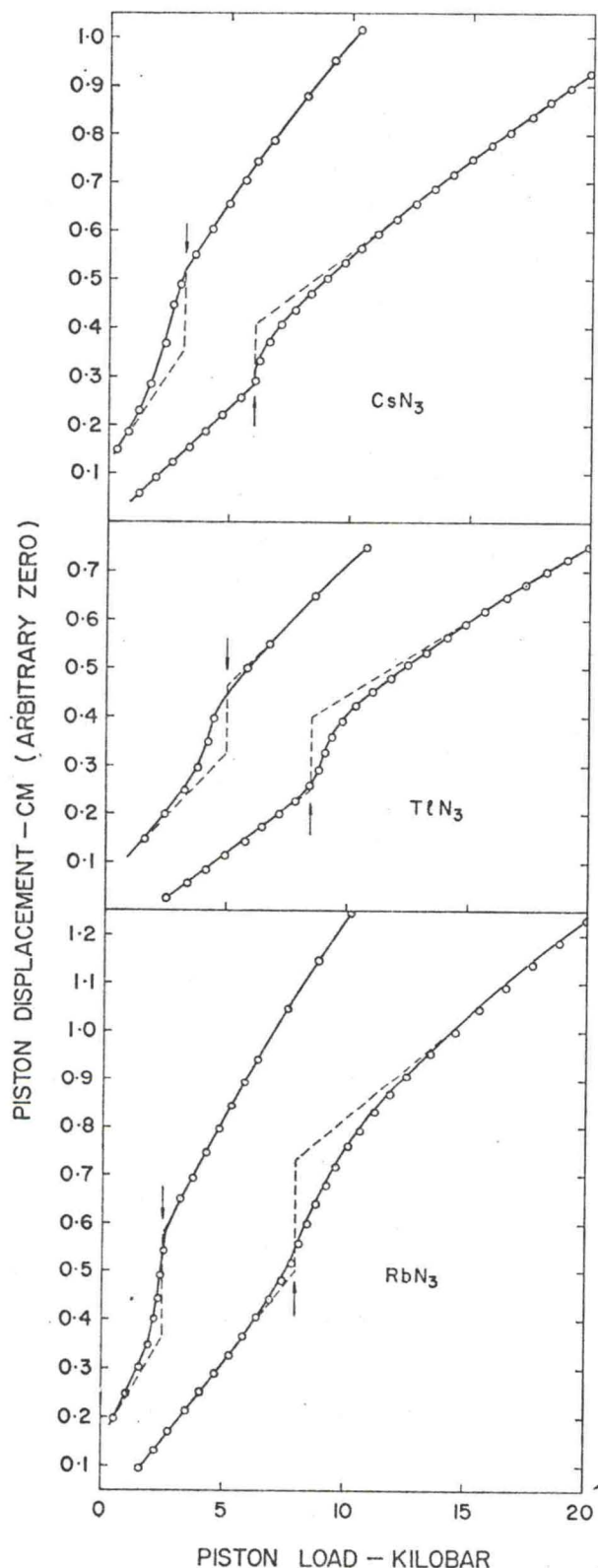
FIG. 3. Curves of piston displacement versus piston load for CsN₃, TlN₃, and RbN₃, showing the new high-pressure transformations. The results are not corrected for the compression of the talc fillers and the deformation of the pressure vessel. The dashed lines indicate the idealized curves to be expected if the measurements were made at a sufficiently slow rate.

peratures above room temperature could be obtained by wrapping a heating coil around the pressure plate.

RESULTS

Cesium Azide

The phase diagram of CsN_3 is shown in Fig. 2. The II–I transition yielded sharp DTA signals [Fig. 1(a)] with less than 2°C hysteresis between heating and cooling for heating/cooling rates ranging from 0.3–1.2°C/sec. Our room-pressure transition temperature was 141.0±1.0°C, being the mean of 26 determinations. This value is considerably lower than that obtained previously[7] in a petrographic microscope, viz., 151°C. The transition line rises with pressure with a slope of 3.96°C/kbar to a triple point CsN_3 I/III/II at 173°C, 8.0 kbar. At this point the DTA signals abruptly change from sharp to smeared [Fig. 1(b)], and the thermal hysteresis increases from ~1 to ~4°C, thereafter decreasing slowly at higher pressures. In addition the slope of the transition line increases to ~13°C/kbar. The III–I boundary was followed to 37 kbar, where the transition temperature was 431°C. A search was made by means of volume displacement for the expected CsN_3 II–III high-pressure transformation at room temperature, and it was easily observed with a volume change of 4.2% [Fig. 3]. By means of piston rotation the transition pressure at 25.7°C was found to be 4.09±0.42 kbar, yielding a slope of 38°C/kbar for the transition line. This implies that CsN_3 II should transform to CsN_3 III upon cooling at atmospheric pressure near −130°C, if the transition line has negligible curvature. The thermodynamic details of the high-pressure transition are given in Table I. No reliable signals were obtained on the melting curve of CsN_3 I, possibly because of slow decomposition while approaching the melting curve. The phase relations of CsN_3 are summarized in Table II. The polymorphic phase boundaries were fitted to simple power series.

The entropy change at the CsN_3 II–I transition is 1.8 cal/mole degree.[7] The Clapeyron relation together with the present initial slope of the transition line then yields

$$\Delta V_{II/I} = 0.30 \text{ cm}^3/\text{mole}.$$

If it is assumed that the entropy of the II–I and II–III transitions remain approximately constant along the respective transition lines, the entropy of the III–I transition is 3.1 cal/mole·deg. The slope of this line is 12.9°C/kbar at the triple point, and this yields

$$\Delta V_{III/I} = 1.7 \text{ cm}^3/\text{mole at 8.0 kbar}.$$

This result, in turn, suggests that $\Delta V_{III/II}$ decreases with increasing transition temperature, as is usual.

TABLE I. Thermodynamic details of the high-pressure transitions.

Boundary	dT/dP_{obs}	ΔV_{obs} (cm³/mole)	ΔS_{calc}[a] (cal/mole·deg)	Estimated transition temperature at 1 bar
CsN₃ II/III	38°C/kbar	−2.1	−1.3	−130°C
TlN₃ II/III	16.5°C/kbar	−1.8	−2.6	−80°C
RbN₃ II/III	41.7°C/kbar	−1.5	−0.9	−200°C

[a] Calculated from Columns 2 and 3 by application of the Clapeyron relation.

Thallous Azide

The phase diagram of TlN₃ is shown in Fig. 4. The II–I transition yielded sharp DTA signals [Fig. 1(c)] with 2–3°C thermal hysteresis at heating/cooling rates ranging from 0.2–1.1°C/sec. The thermal hysteresis decreases slowly at higher pressures to ∼0.5°C at 20 kbar. Our room-pressure transition temperatures were 292.0°C (heating) and 289.3°C (cooling), being the mean of 14 determinations. This value is in fair agreement with the previous DTA value[3] of 295°C. The II–I transition line was followed only to 20 kbar, where it is terminated by explosive decomposition. The explosions were sufficiently violent to raise the pressure on the sample by ∼6 kbar. The melting curve of

FIG. 4. Phase diagram of TlN₃ to 20 kbar.

TlN₃ I was followed only to 4.5 kbar, 410°C. Attempts to melt TlN₃ at higher pressures resulted in explosive decomposition. The DTA signal shown in Fig. 1(d) is typical of the melting of also TlN₃.

A search was made by means of volume displacement for a possible high-pressure transformation in TlN₃ similar to the CsN₃ II–III transition. The curves are shown in Fig. 3. The transition has a volume change of 3.2%. By means of piston rotation the transition pressure at 29°C was found to be 6.65±0.83 kbar, and 10.88±0.58 kbar at 98.5°C, yielding a considerably lower slope than in the case of CsN₃ II–III. The thermodynamic details of the high-pressure transition are given in Table I, while the phase relations of TlN₃ are summarized in Table II. The melting curve is fitted to the Simon equation[17]

$$P = A[(T/T_0)^c - 1],$$

where $T(°K)$ and $T_0(°K)$ are the melting points at P kbar and atmospheric pressure, respectively. A and c are adjustable constants, determined by means of Babb's method.[18]

The entropy change at the TlN₃ II–I transition is 1.0 cal/mole·deg.[8] This yields

$$\Delta V_{II/I} = 0.44 \text{ cm}^3/\text{mole}.$$

Rubidium Azide

A portion of the phase diagram of RbN₃ is shown in Fig. 5. Experimental work on the II–I boundary and the melting curve was made difficult by the proximity of the transition temperature (315°C) and the melting point (317°C), and it was not possible to separate these changes at elevated pressures. At 4.1 kbar the transition was not observed at all, but a clear melting signal occurred at 453°C, followed by explosive decomposition at ∼460°C. The suggested boundaries of Fig. 5 are drawn to suggest a triple point RbN₃ liq/II/I near 1–2 kbar. Further work on these boundaries should be carried out in completely hydrostatic pressure devices.

A high-pressure transition RbN₃ II–III was found by means of volume-displacement techniques. The
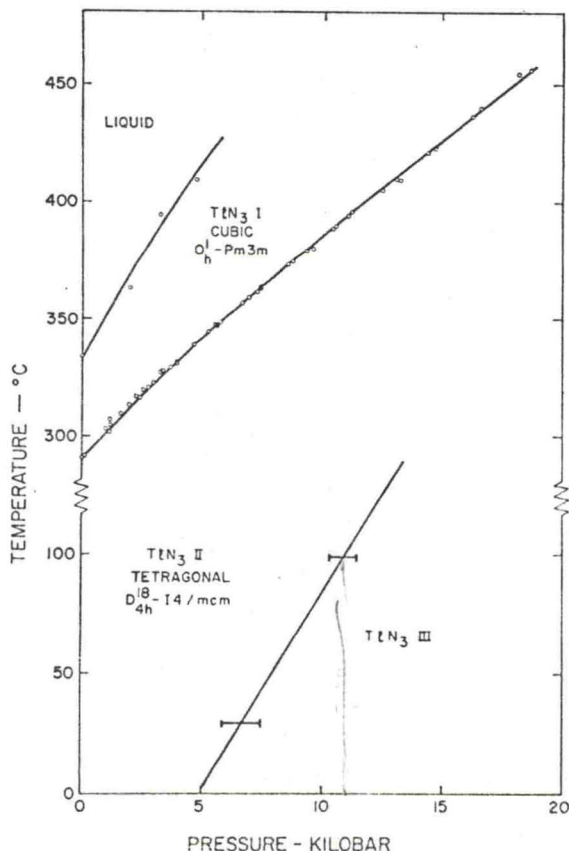
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TABLE II. Phase behavior of the azides.

Boundary	Fit (P in kbar)	Standard deviation
CsN$_3$ I/II	$t(°C) = 141.0 + 3.96\,P$	1.3°C
CsN$_3$ I/III	$t = 173 + 12.86(P-8.0) - 0.137(P-8.0)^2$	4.7°C
CsN$_3$ II/III	$P = 3.41 + 0.0265\,t$	···
TlN$_3$ I/liq	$P/24.8 = [T(°K)/607]^{1.426} - 1$	4.9°C
TlN$_3$ I/II	$t(°C) = 290.6 + 10.59\,P - 0.0994\,P^2$	1.9°C
TlN$_3$ II/III	$P = 4.90 + 0.0607\,t$	···
RbN$_3$ II/III	$P = 4.82 + 0.0240\,t$	···
KN$_3$ sol/liq	$P/2.45 = (T/618)^{10.63} - 1$	1.7°C

transition is considerably more sluggish than the corresponding transitions in CsN$_3$ and TlN$_3$ (Fig. 3) and has a volume change of $\sim$3.4%. However, it becomes less sluggish at higher temperatures. The transition pressures shown in Fig. 5 were determined by means of piston rotation. The slope of the transition line is 41.7°C/kbar, closely the same as that of the CsN$_3$ II–III transition.

Potassium Azide

The melting curve of KN$_3$ is shown in Fig. 6. A typical melting signal is shown in Fig. 1(d). In order to prevent explosive decomposition as far as possible, heating was stopped as soon as the melting signal was observed. However, the melting curve is terminated near 3.3 kbar, 396°C, with exposive decomposition.

A search was made for a possible high-pressure transition at 19°C, but with negative results. However, a transition below $\sim$2 kbar would not have been recognized by means of our methods, and in view of the close similarity between the azides studied here it is suggested that a high-pressure transition may occur at very low pressures.

DISCUSSION

The volume changes of the tetragonal/cubic high-temperature transitions in CsN$_3$ and TlN$_3$, as found here, are very small, being of the order of 0.4 cm^3/mole as compared to a total change of $\sim$6 cm^3/mole[7] due to thermal expansion from 25–290°C. This implies that
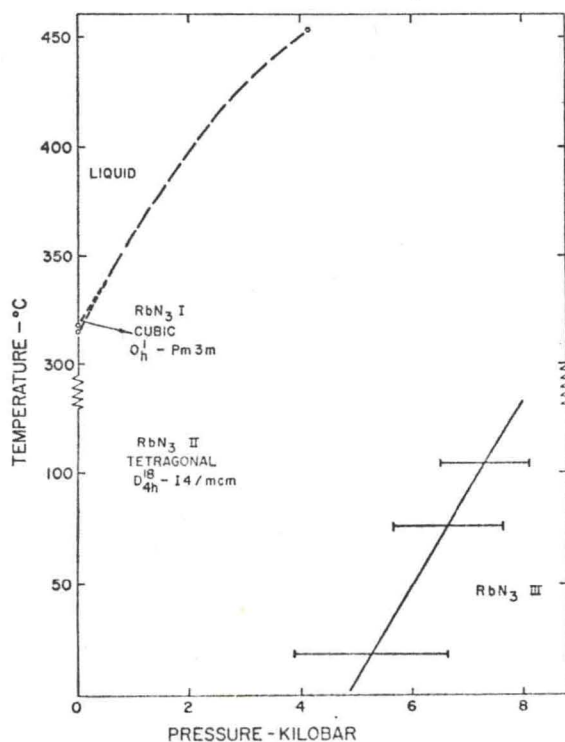

FIG. 5. Phase diagram of RbN$_3$ to 8 kbar. Dashed lines indicate estimated boundaries.
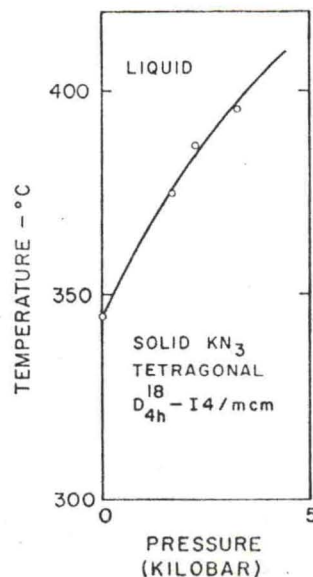

FIG. 6. The melting curve of KN$_3$ to 5 kbar.

the disordering of the lattice is primarily dictated by geometrical considerations, with thermal agitation having a secondary role, and may explain the linear dependence[7] of the transition temperatures on the cation radii. To a good approximation, therefore, the transition occurs as soon as the lattice has sufficiently expanded to allow random orientation of the azide ions along the edges of the cubic unit cell, without a large discontinuous decrease in density being necessary.

The entropy of the II–I transition for CsN_3 and RbN_3 (1.9 cal/mole·deg) is considerably higher than that for TlN_3 (1.0 cal/mole·deg). Mueller and Joebstl[7] pointed out that the theoretical transition entropy, assuming completely random orientation of the azide ions parallel to the edges of the unit cell, is 2.13 cal/mole·deg. However, since the length of the azide group ($\sim$5.09 Å) is slightly greater than the cubic unit-cell dimension for CsN_3 I (4.53 Å at 290°C), it can be expected that the alignment of two or more adjacent azide ions in the same direction is improbable. The exclusion of the less probable alignment of three azide ions was sufficient to obtain a theoretical entropy change of 1.96 cal/mole·deg, in good agreement with experiment. The very low value of 1.0 cal/mole·deg for TlN_3 may possibly be ascribed to the known high polarizability of the thallous ion, which will have the effect of decreasing the randomness of the azide ions in TlN_3 I still further, and thereby lowering the transition entropy.

The similarity in behavior of the new high-pressure transitions in CsN_3, TlN_3, and RbN_3 (Fig. 3 and Table I) strongly suggests that these high-pressure phases are isostructural. It can be seen in Table I that the entropy of the transition for CsN_3 and RbN_3 is close to $R\ln2$ (1.38 cal/mole·deg), while in the case of TlN_3 it is close to $R\ln3$ (2.18 cal/mole·deg). The high-pressure phases have the lower entropy in all cases. A value of $R\ln2$ is simply explained by postulating that in the high-pressure phase pairs of crystallographically nonequivalent azide ions occur, while in the low-pressure phase, as is known, all azide ions are equivalent. Two different structures of this type are known, viz., that of NH_4N_3[19] and that of AgN_3.[20] If a plot is made of unit-cell volumes against cation radii for all the azides with one of these structures or the KN_3 structure, it is found that the data for the isomorphous

series of tetragonal azides lie on a straight line, while the latter two structures are considerably more densely packed. They are therefore possible high-pressure structures with respect to the tetragonal KN_3 structure. The higher entropy difference for TlN_3, assuming that TlN_3 III has the same structure as CsN_3 III, can possibly be explained as due to a vibrational entropy contribution since it can be expected that the vibrational entropy term is much more sensitive to geometrical changes for lattices containing highly polarizable atoms.

The low-temperature phases of KHF_2, $RbHF_2$, and $CsHF_2$ have the tetragonal KN_3 structure.[21] The high-temperature phase of $CsHF_2$ has the same structure as the high-temperature phase of CsN_3, but the high-temperature phases of KHF_2 and $RbHF_2$ have a structure related to that of NaCl instead of CsCl.[21] The HF_2^- ions are aligned along randomly chosen body diagonals of the unit cube, with the centers of the ions in symmetry positions. The phase diagrams of KHF_2 and $RbHF_2$ can therefore be expected to be made up of this tetragonal/fcc transition line, which will, probably at quite a low pressure, be terminated in a triple point with the appearance of a denser high-pressure high-temperature phase with the CsN_3 I structure. At higher pressures there will therefore be a tetragonal/bcc transition line with a low slope and a bcc/fcc transition line with a high slope. At higher pressures and low temperatures a further transition to a CsN_3 III-like phase may be expected. Work is in progress to study the phase diagrams of these substances.

ACKNOWLEDGMENTS

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