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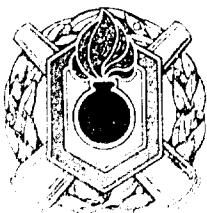
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DISCOVERY OF A LOW TEMPERATURE FORM OF TAGN

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19. ABSTRACT (CONTINUE ON REVERSE IF NECESSARY AND IDENTIFY BY BLOCK NUMBER) <i>Continued from page 1</i> A low temperature polymorph of trisaminoguanidinium nitrate (TAGN) was discovered by this laboratory during the course of a rigid-body motion study of the nitrate ion. Differential scanning calorimetry (DSC) measurements made at several different heating rates over a temperature range of -100 degrees C to room temperature yielded a small reversible endotherm with a reproducible onset temperature and reproducible heat capacity values. X-ray diffraction measurements also were carried out over a similar temperature range to determine the relationships among reflection intensity, lattice parameters (unit-cell volume), and temperature. Details of the experimental procedures, results, and implications are presented. <i>Key words: TAGN</i>				
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INTRODUCTION

Start here
Triaminoguanidinium nitrate (TAGN) has been frequently added to cyclic nitramine (RDX) propellant formulations in an effort to increase the burning rates of these propellants. This is particularly important in LOVA propellants formulated for high performance artillery or tank gun applications where faster burning rates are necessary. Although this property of TAGN was known for quite some time, no satisfactory explanation for this phenomenon presently exists. In an effort to understand this compound and its properties more completely, a room temperature single crystal x-ray diffraction study was initiated by this laboratory (ref 1) followed by a neutron diffraction study at another Picatinny Arsenal facility (ref 2).

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One of the more interesting things revealed by the studies was the presence of nitrate ion disorder. That observation was based on the extremely large thermal vibrations displayed by the oxygen atoms of the nitrate ion. This disorder was explained on the basis of rigid-body motion (libration) in which the nitrate ion was assumed to behave as a rigid rotor hindered from free rotation by the forces of hydrogen bonding. This dynamic disorder can be described by picturing this planar ion as a continuously oscillating pin-wheel containing an oxygen atom on the terminus of each of three spokes (an oxygen triad) and an axis of rotation that passes through the central nitrogen atom normal to the ionic plane.

On the other hand, positional disorder could also account for these unusually large observed thermal amplitudes. In this case, the oxygen atoms would be distributed over several partially filled positions that are related by three-fold rotational symmetry to the central nitrogen atom. The distinction between the two explanations for the observed disorder is quite subtle because rigid-body motion would be required at some temperature to induce this type of positional disorder. Positional disorder is a static phenomenon which results when moving atoms at a given temperature are frozen in fixed positions at some lower temperature. Therefore, the resolution of this question would be academic were it not for the interest in knowing at what temperature molecular motion begins. Since rigid-body motion should occur in the nitrate ion at some temperature, it seems quite probable that as the crystal temperature is lowered, rigid-body motion should decrease until a sufficiently lower temperature is reached where libration ceases (freeze-out temperature).

If all the oxygen triads throughout the crystal are identically oriented when motion stops, the resulting structure is ordered and the thermal amplitudes should be no longer extraordinarily large. This is referred to as an order-disorder transition. Furthermore, this transition is reversible because rigid-body motion will resume as the temperature is raised.

Conversely, if all the oxygen triads freeze out but not in precisely the same orientation, positional disorder results and extremely large thermal amplitudes will still prevail. The degree of disorder and the magnitude of the resulting thermal amplitudes will depend on the orientation of the sets of oxygen triads. In the extreme case, random orientation of the oxygen triad sets within the ionic plane would result in maximum positional disorder which is analogous to free rotation in dynamic disorder. Further lowering of the temperature beyond freeze-out will have

no effect upon the disorder unless there is also a polymorphic transition (change in crystal structure).

In an effort to resolve the question whether the observed room temperature disorder was positional or dynamic, the crystal structure was redetermined utilizing a positional disorder model (ref 3). Although the results were not definitive, they suggested that at room temperature librational motion in the nitrate ion was probably the most correct explanation for the observed disorder. It was also recommended that low temperature thermal and molecular structure investigations be carried out in order to unequivocally ascertain both the nature of room temperature disorder in TAGN and the freeze-out or transition temperature. As a result, low temperature DSC and x-ray diffraction studies were initiated by this laboratory.

DISCUSSION

Data Collection

A colorless crystal of TAGN (approximate dimensions 0.10 x 0.15 x 0.30 mm) was mounted on a glass fiber with its long axis approximately parallel with the ϕ axis of the goniometer. Preliminary examination and data collection were performed over the temperature range of -100 to 15°C with Mo K x-radiation ($\lambda = 0.71073$ Å) on an Enraf-Nonius CAD4 computer controlled kappa axis x-ray diffractometer equipped with a graphite crystal incident beam monochromator.

The cell constants and an orientation matrix for data collection were obtained from least-squares refinement, using the setting angles of 25 reflections in the range $4 < \theta < 8$, measured by the computer controlled diagonal slit method of centering. The orthorhombic cell parameters and volumes were determined over the specified temperature range.

Three reflections were selected to monitor the effect of temperature on intensity. Two of the reflections [$I(102)$ and $I(7 -2 1)$] were selected because they were present only below -10°C while the third reflection ($0 -2 1$) was selected because it was present over the entire temperature range and had an interplanar distance equivalent to $(7 -2 1)$. The interplanar distances (d spacings) for $d(102)$, $d(7 -2 1)$, and $d(0 -2 1)$ are 33.221(2), 10.210(4), and 9.058(4) Å, respectively.

The Dupont 1090 thermal analyzer in conjunction with the 910 DSC cell was used to determine the heat capacity of TAGN over the temperature range of -70 to 100°C (table 3). Sample sizes ranging from 5 to 10 mg were examined at a heating rate of 20°C/min. This report will only address the thermal events occurring over the range of -100°C to ambient.

X-Ray Data

The lattice parameters data (table 1) reveal the existence of a low temperature form of TAGN with b and c axes similar to those of the room temperature form but whose a axis had increased fourfold. As this form is heated from -100 to 55°C, the unit cell expands anisotropically with the

a axis increasing about 1.0%, b about 0.4%, and c about 0.5%. This gradual expansion of the unit cell is usually observed when solids are heated. Continued heating to 23°C results in a similar expansion trend only for the b and c axes (0.5% and 0.6%, respectively). The a axis, however, contracts quite suddenly to 1/4 of its value, indicating a polymorphic phase transition. The temperature versus lattice parameter curves (figs. 1 and 2) clearly illustrate the effect of temperature on unit-cell dimensions. The plot of Δ /deg versus T (fig. 3) reveals the transition temperature to be about -10°C.

Both polymorphs have the same orthorhombic point group symmetry (mmm D_{2h}) with the low temperature form crystallizing in the space group Pbc₂a and the high temperature form belonging to Pbcm.

The integrated intensity values for three reflections [I (102), I (7 -2 1), and I (0 -2 1)] measured over the temperature range of -100 to 15°C (table 2) reveal that the effect of temperature on diffraction intensity is not the same for each reflection. For the (0 -2 1) reflection, the intensity is lowest (2400 counts) at -100°C then rises to the 3000-count level where it stays constant (within experimental accuracy) over the remainder of the temperature range (fig. 4). This indicates that the set of atomic planes is relatively unaffected by temperature which suggested there is little or no significant increase in atomic (thermal) motion in this temperature range for the atoms in (0 -2 1).

Conversely, with the other two reflections (figs. 5 and 6), intensity decreases between -100 and -55°C then decreases more rapidly until it becomes zero at the transition point where these lattice planes become nonexistent. The intensity decrease is probably caused by the increase in temperature dependent atomic motion in the (102) and (7 -2 1) planes of the low temperature form.

Since the interplanar distances of these reflections (10 to 33 Å) are very large, the relatively small internal atomic thermal vibrations should have minimal effect on their diffraction intensities. This means the intensity attenuation observed for both I(102) and I(7 -2 1) must be caused by molecular motion (rigid body).

Thermal Data

A typical TAGN DSC heating curve for the temperature range -100 to 20°C is presented in figure 7, in which several well defined features are evident. Initially, between -100 and -55°C, the curve displays a negative slope until -55°C where the slope becomes more steeply negative; at about -25°C, the onset of an endotherm with a -10°C peak temperature ($\Delta H = 0.1(1)$ kcal/mole) occurs. This correlates quite well with x-ray intensity data for I(102) and I(7 -2 1), and with the contraction of a axis. At about 0°C, the base line curve resumes with the same negative slope initially observed.

Oyumi reported two small endotherms in this temperature range, one at -10°C [$\Delta H = 0.4(1)$ kcal/mole] and a smaller one at -3°C [$\Delta H = 0.3(1)$ kcal/mole] utilizing differential thermal

analysis (DTA) (ref 4). The absence of the smaller endotherm in this study may reflect the difference in sensitivity between the two techniques rather than any real difference in data.

The plot of heat capacity versus temperature (fig. 8) indicates that the heat capacity remains constant (1.33 J/g) until -55°C is reached, then increases with temperature until approximately -15°C where a small exotherm or second order transition appears with a peak at -10°C . After this peak, the heat capacity resumes its direct relationship with temperature. Although the post-peak base line has shifted upward, it has the same slope as the pre-peak base line.

CONCLUSIONS

The x-ray diffraction data reveal the following significant facts:

1. There is a polymorphic phase transition near -10°C
2. The space group of the low temperature form is Pbcn and the space group of the high temperature form is Pbcm
3. Those reflections unique to the low form are attenuated with increasing temperature
4. At temperatures greater than -55°C , the rate of intensity attenuation increases

The thermal data reveal that:

1. Heat capacity (C_p) is relatively constant from -100 to 55°C
2. Heat capacity increases in the temperature range of -55 to 60°C
3. There is a polymorphic phase transition at -10°C
4. The transition is second order

These revelations suggest that at -55°C restricted libration (probably oscillation of the nitrate ion) either begins or increases until the broad second order transition takes place. Pauling (ref 5) and Fowler (ref 6) have theorized that a second-order transition in heat capacity can be caused by the transition from molecular oscillation to free rotation. Furthermore, only small structural changes accompany a second order transition with the low temperature form (but not necessarily) having the low symmetry.

These observations are consistent with the results obtained in an independent IR study (ref 4) in which the internal modes were found to be unaffected by the phase transition indicating very subtle structural changes. The linewidths also were unchanged down to -90°C which suggested that librational motion was in effect down to this temperature.

Phase changes can alter physical properties which sometimes cause serious problems in propellant formulations. If, for example, the polymorphs of a propellant ingredient have very different densities, substantial expansion and contraction can occur during temperature cycling which may initiate crack formation in propellant grains. Since the transition of TAGN is well within the temperature variation experienced by propellants, the physical properties of the low temperature form could affect the propellant if they differ significantly with those of the room temperature form. The potential effects of this transition on propellants, however, cannot be determined until the low temperature form has been characterized.

RECOMMENDATIONS

Future work should be directed toward characterizing the low temperature form. This should include a low temperature structure determination and thermal studies at lower temperatures and higher pressures.

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Table 1. TAGN lattice parameters and their estimated standard deviations as a function of temperature

Temperature (°C)	Parameters			
	a (Å°)	b (Å°)	c (Å°)	v (Å°)
-100	33.07(1)	12.581(4)	6.518(3)	2711.8
-64	33.199(4)	12.594(4)	6.537(4)	2732.2
-51	33.245(7)	12.603(3)	6.544(4)	2741.5
-27	33.344(8)	12.622(4)	6.548(2)	2755.5
-26	33.344(9)	12.619(4)	6.546(2)	2754.8
-13	33.408(9)	12.635(3)	6.550(3)	2764.8
^a				
-5	33.444(9) ^b	12.641(4)	6.552(5)	2770.0 ^b
15	33.47(1) ^b	12.659(5)	6.559(3)	2779.0 ^b
23	8.366(2)	12.649(2)	6.556(1)	693.8(1)

^a Transition temperature near -10°C.

^b The a axis and volume above transition temperature are actually 1/4 the value indicated.

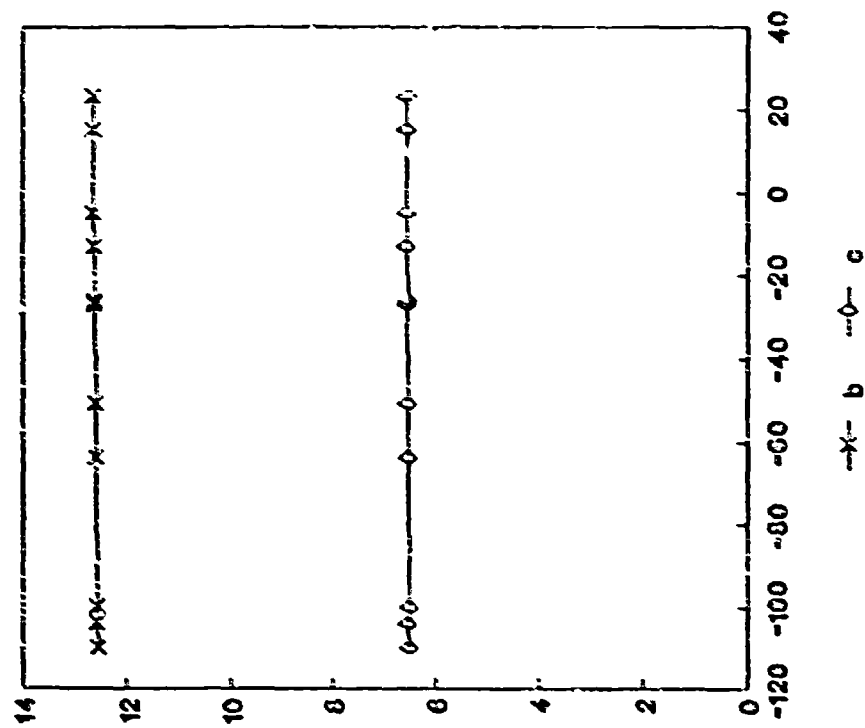
Table 2. Intensity values for the three most intense TAGN x-ray diffraction reflections as a function of temperature

Temperature (°C)	I(102) (counts)	I(7 -2 1) (counts)	I(0 -2 1) (counts)
-100	6445	504	2409
-64	5809	488	2970
-51	5224	352	2933
-27	3137	232	2760
-26	3159	205	3096
-13	1092	65	3200
-5	*	*	2997
15	*	*	3088

* Reflection absent because of phase change near -10°C.

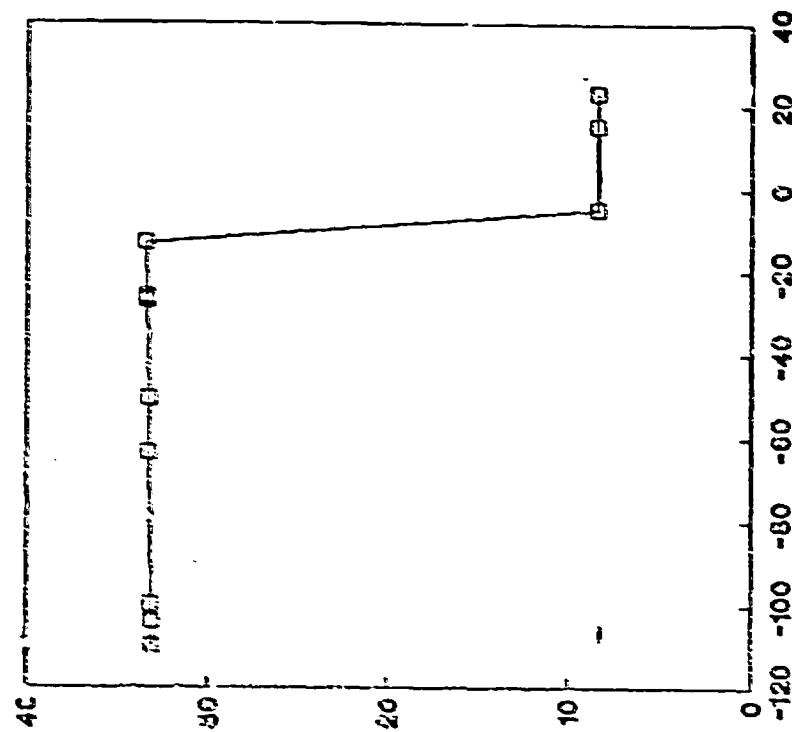
Table 3. Heat capacity of TAGN versus temperature

Temperature (°C)	Heat capacity	
	(J/kg)	(Cal/kg)
-70	1320	0.315
-60	1336	0.319
-50	1360	0.325
-45	1386	0.331
-40	1413	0.338
-35	1441	0.344
-30	1466	0.350
-25	1495	0.357
-20	1525	0.364
-15	1543	0.369
-10	1610	0.385
-5	1570	0.375
0	1539	0.367
5	1559	0.373
10	1586	0.379
20	1634	0.391
30	1688	0.403
40	1752	0.414
50	1781	0.426
60	1811	0.433
70	1842	0.440
80	1881	0.450
90	1943	0.456
100	1959	0.460



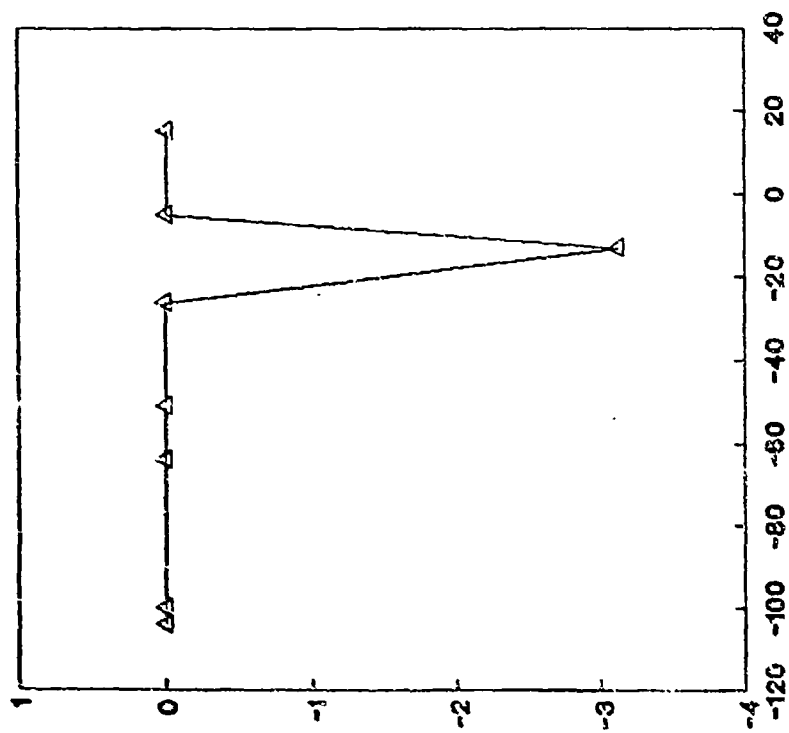
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Figure 1. Plot of unit-cell dimension (b and c) versus temperature



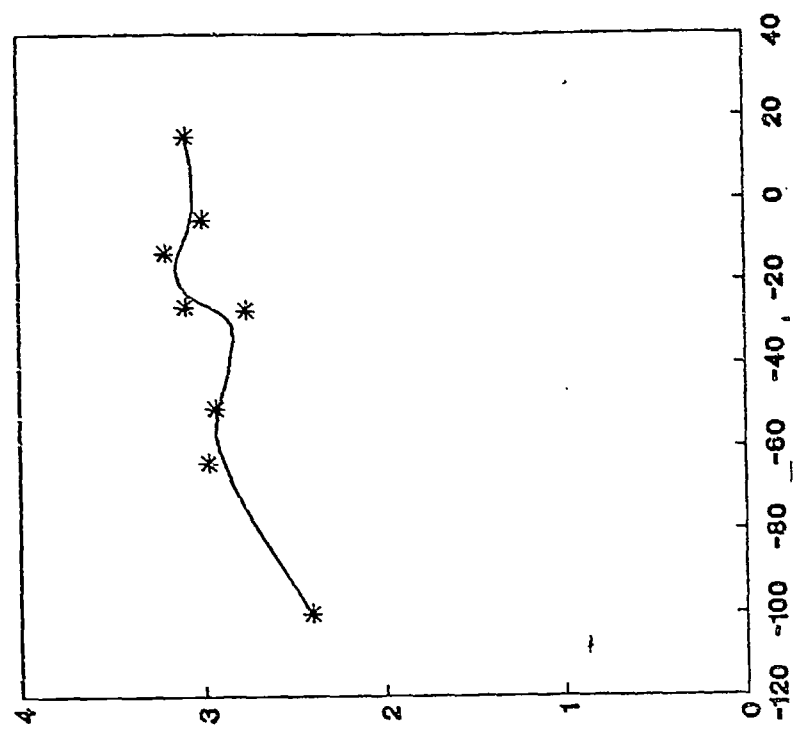
Temperature, °C

Figure 2. Plot of unit-cell dimensions (a) versus temperature



Temperature, °C

Figure 3. Plot of $\Delta a / \Delta T$ versus temperature



Temperature, °C

Figure 4. Plot of intensity of reflection (0-21) versus temperature for TAGN

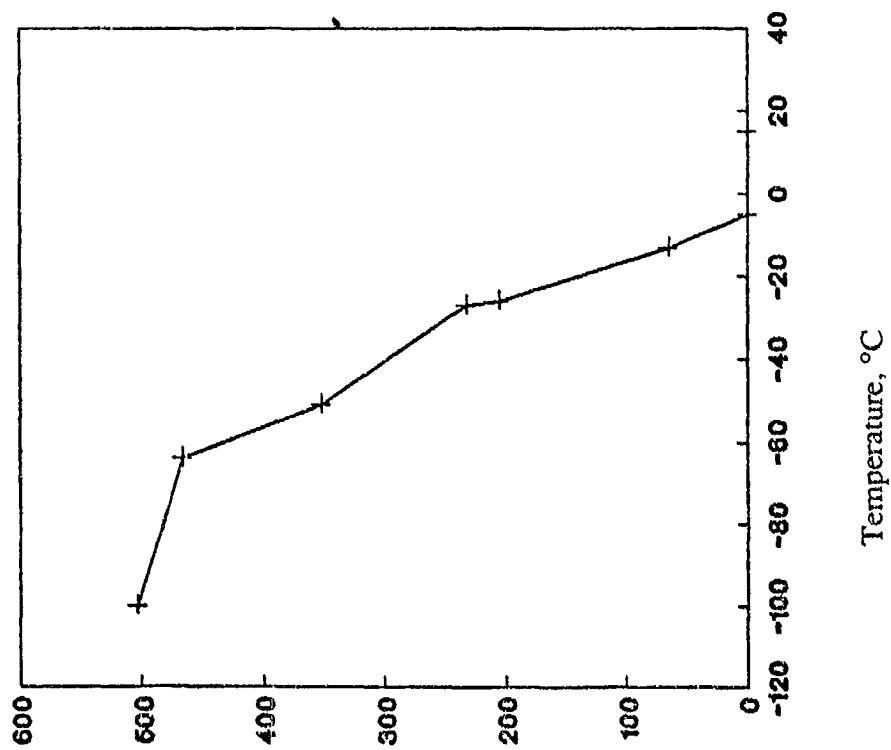


Figure 5. Plot of intensity of reflection (7-2-1) versus temperature for TAGN

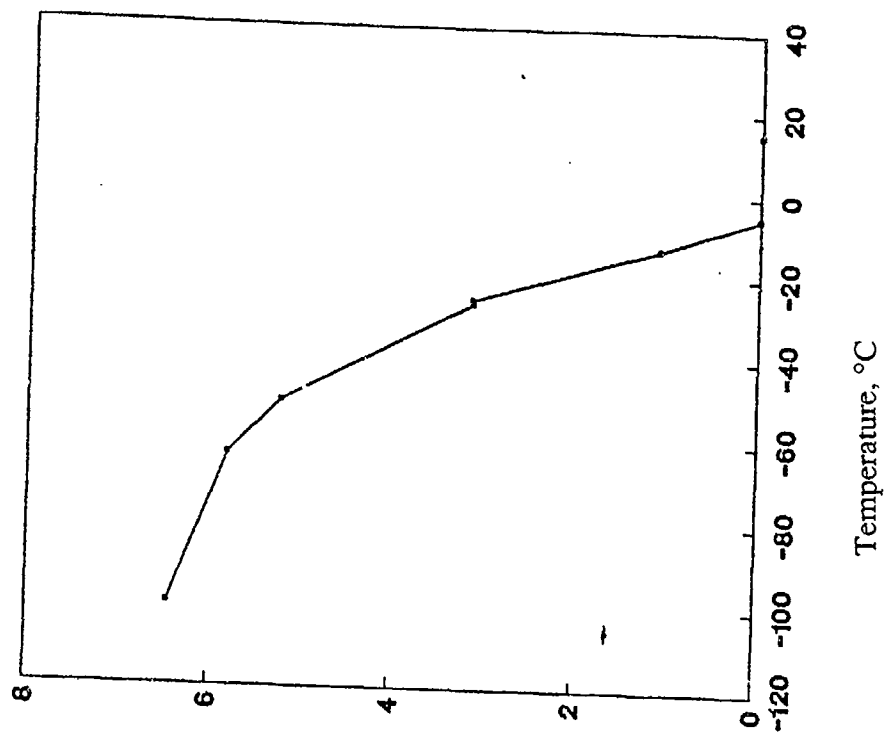


Figure 6. Plot of intensity of reflection (1 0 2) versus temperature for TAGN

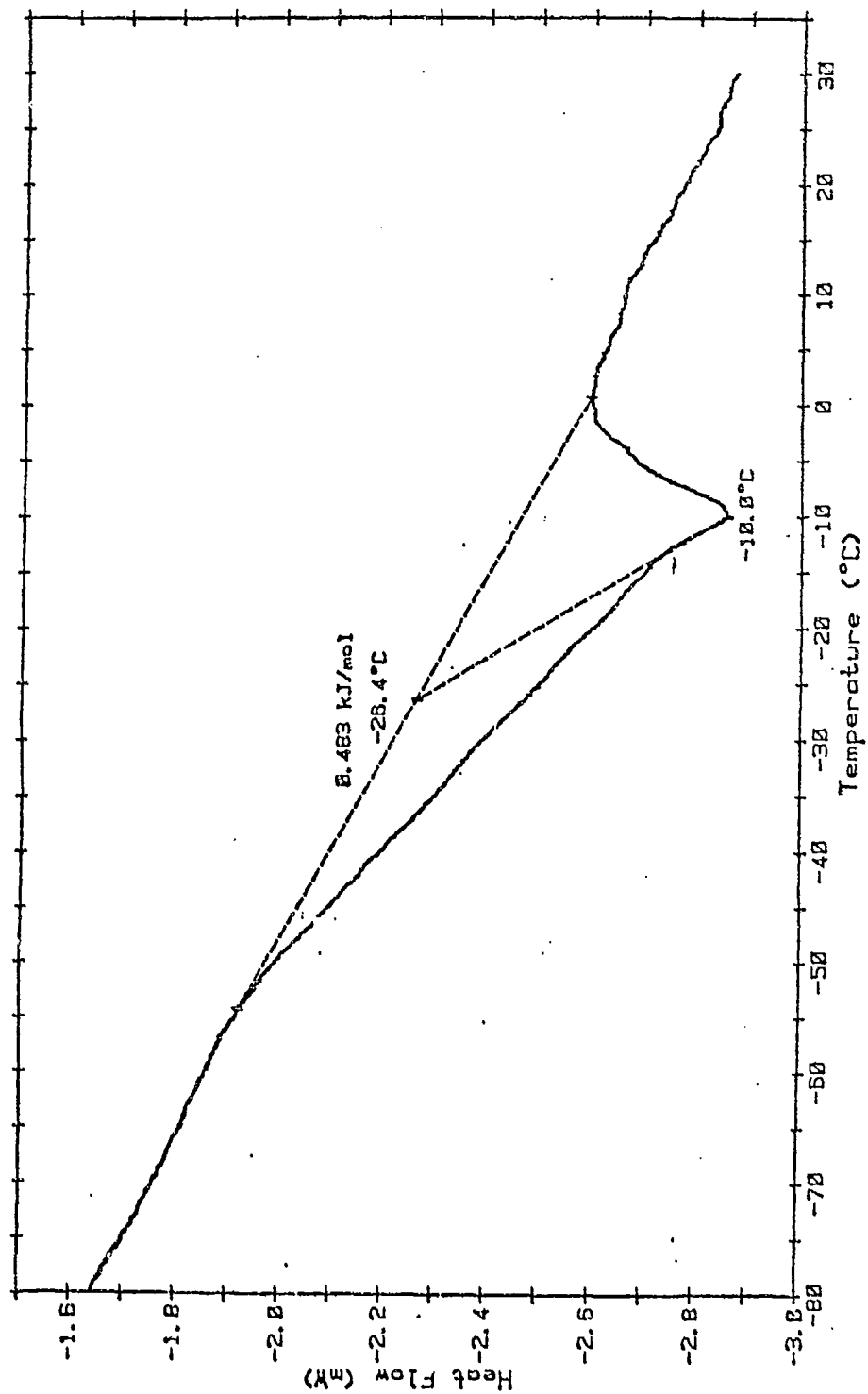


Figure 7. DSC thermogram of TAGN

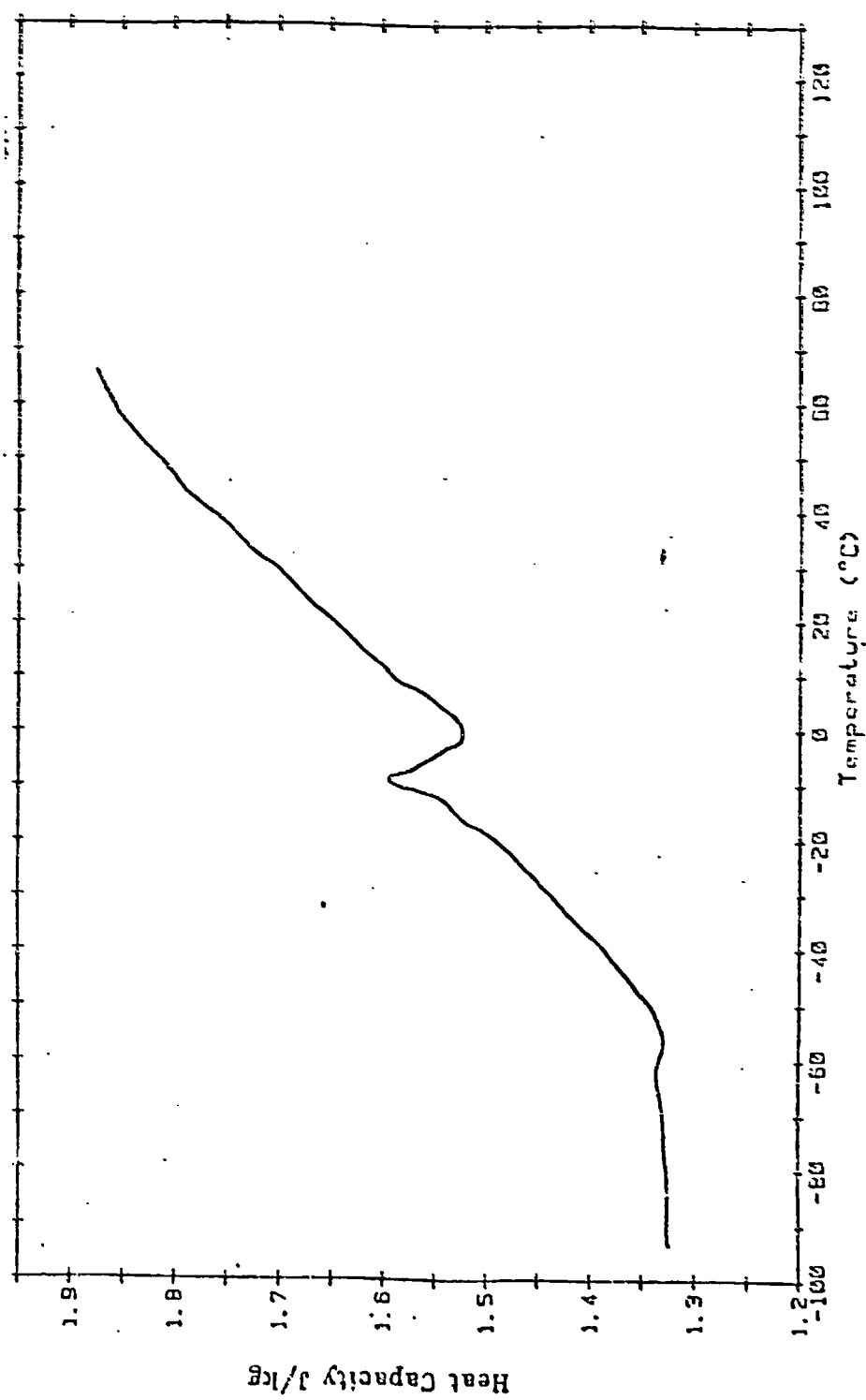


Figure 8. Heat capacity curve for TAGN as a function of temperature

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