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J. Chem. Thermodynamics **1992,** 24, 1001–1007

Thermodynamics of ammonium halopallidates

I. Heat capacity and thermodynamic properties of $(NH_4)_2PdCl_6$ at temperatures from 6 K to 350 K

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(Received 28 January 1992; in final form 3 March 1992)

The heat capacity of ammonium hexachloropallidate $(NH_4)_2PdCl_6$ was measured at temperatures from 6 K to 350 K by adiabatic calorimetry. The heat-capacity curve is smooth and without anomalies. It rises rapidly from $T \rightarrow 0$ to $T = 150$ K where the $C_{p,m}$ value is $26.62 \cdot R$ ($R = 8.31451\ J \cdot K^{-1} \cdot mol^{-1}$). Above $T = 150$ K, the increase to $32.41 \cdot R$ at 350 K occurs more slowly. Values of the standard thermodynamioc quantities are tabulated to $T = 350$ K.

1. Introduction

The ammonium hexahalogenated metallates $(NH_4)_2MX_6$ (M denotes a polyvalent ion, and X denotes a halogen) usually crystallize at room temperature into a cubic antifluorite structure of space group $Fm\bar{3}m$ and are ideal models for studying molecular motion in solids. The NH_4^+ ion, located at a tetrahedral lattice site, is able to overcome the low barrier to rotation about its threefold axis. At room temperature, NH_4^+ experiences classical hindered rotation and, at $T < 40$ K, quantum-tunnelling.[1] Some salts in this family undergo structural phase transitions and change into a phase of lower symmetry as the temperature is lowered.[2] Some

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0021–9614/92/091001+07 $02.00/0

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salt pairs, *e.g.* K_2SnCl_6, $(NH_4)_2SnCl_6$,[3] and K_2OsCl_6,[4,5] $(NH_4)_2OsCl_6$,[6] show evidence of a transition in the alkali salt but not in the ammoniated salt. The $(NH_4)_2PtCl_6$,[7] $(ND_4)_2PtCl_6$,[8] pair is an example where a structural transition occurs only in the deuterated analogue. However, in the tellurium salts, there is a single structural transition in $(NH_4)_2TeCl_6$,[9] but there are two additional transitions in $(ND_4)_2TeCl_6$.[10,11]

Low barriers to rotation of $342 \cdot R \cdot K$ and $307 \cdot R \cdot K$ have been reported[12] for NH_4^+ in $(NH_4)_2PtCl_6$ and $(NH_4)_2PdCl_6$, respectively, which have attracted interest in determining the rotational potential of NH_4^+ in these and related compounds.[13-16] Heat-capacity results, a knowledge of which should help in understanding the mechanism of molecular rotation, are not available for either $(NH_4)_2PdCl_6$ or its deuterated analogue. We have, therefore, measured the heat capacity of $(NH_4)_2PdCl_6$ at temperatures from 6 K to 350 K by adiabatic calorimetry as part of our ongoing work with ammonium salts, and the results are described below.

2. Experimental

The sample of $(NH_4)_2PdCl_6$ was supplied by the Aldrich Chemical Company as 99.99 mass per cent pure according to the Certificate of Analysis. The only other element detected by spectrographic trace analysis was Fe with mass fraction $6 \cdot 10^{-6}$. The finely-divided red powder was used as supplied as there was no need to grind the sample further.

The Guinier–de-Wolff diffraction pattern of our sample was in perfect agreement with the standard pattern for this compound: No. 9-397 as determined by the Joint Committee for Powder Diffraction Standards.[17] The structure at room temperature is face-centred with $a = (0.9819 \pm 0.0006)$ nm, which compares with 0.9826 nm for the standard.[17]

The molar heat capacity $C_{p,m}$ was measured from $T = 6$ K to $T = 350$ K by adiabatic calorimetry in the Mark XIII adiabatic cryostat described previously.[18] A guard shield was incorporated to surround the adiabatic shield. A Leeds and Northrup capsule-type platinum resistance thermometer (laboratory designation A-5) was used for the temperature measurements. The thermometer was calibrated at the U.S. National Bureau of Standards (N.B.S., now NIST) against the IPTS-48 (as revised in 1960)[19] for temperatures above 90 K, against the N.B.S. (NIST) provisional scale from 10 K to 90 K, and by the technique of McCrackin and Chang[20] below 10 K. These calibrations are estimated to reproduce thermodynamic temperatures to within 0.03 K between 10 K and 90 K and within 0.04 K above 90 K.[21] The effects of changing the temperature scale to ITS-90 vary over the range $90 \leqslant T/K < 350$ from $0.020 \leqslant (T_{90} - T_{48})/K \leqslant -0.27$, and for the range $14 \leqslant T/K \leqslant 350$ from $-0.008 \leqslant (T_{90} - T_{55})/K \leqslant 0.018$.[22,23] The changes in heat capacity, enthalpy, and entropy resulting from the conversion from IPTS-68 to ITS-90 have been shown for a number of materials to lie within the experimental error of the measurements over the range from 16 K to 2800 K.[22] Measurements of mass, current, potential difference, and time were based upon calibrations done at N.B.S.

(NIST). The heat capacities from about $T = 6$ K to $T = 350$ K were acquired with the assistance of a computer, which was programmed for a series of determinations.[24,25] During the drift periods, both the calorimeter temperature and its first and second derivatives of temperature with respect to time were recorded to establish the equilibrium temperature of the calorimeter before and after the energy input. While the calorimeter was operating, the heater current and potential difference as well as the duration of the heating interval were determined. Also recorded was the apparent heat capacity of the system, which included the calorimeter, heater, thermometer, and sample.

A gold-plated copper calorimeter (laboratory designation W-99) with four internal vertical vanes and a central entrant well for (heater + thermometer) was loaded with $(NH_4)_2PdCl_6$. After loading, the calorimeter was evacuated and pumping was continued for several hours to ensure that moisture was no longer present in the sample. After addition of helium gas to the vessel ($p = 5.1$ kPa at $T = 300$ K) to facilitate thermal equilibration, the calorimeter was then sealed by means of an annealed gold gasket tightly pressed on to the stainless-steel knife edge of the calorimeter top with a screw closure about 5 mm in diameter.

Buoyancy corrections were calculated on the basis of a crystallographic density of $2.492\ g \cdot cm^{-3}$ derived from the unit-cell edge of our sample. The mass of the $(NH_4)_2PdCl_6$ was 11.94644 g ($\triangleq$0.03363176 mol based on its molar mass[26] of $355.2132\ g \cdot mol^{-1}$).

The thermal history of the $(NH_4)_2PdCl_6$ is represented by the following linear array. The arrows denote either cooling or heating, which correspond to the acquisition of the heat-capacity results.

$$300\ K \xrightarrow{3\ h} 206\ K \xrightarrow[\text{Series I}]{1\ h} 218\ K \xrightarrow{16\ h} 56\ K \xrightarrow[\text{Series II}]{48\ h} 347\ K \xrightarrow{24\ h} 6\ K \xrightarrow[\text{Series III}]{10\ h} 75\ K.$$

3. Results and discussion

The experimental molar heat capacities for $(NH_4)_2PdCl_6$ are presented in table 1, where the temperature represents the midpoint of the temperture intervals. The measurements were made in three series covering the range from $T = 6.0$ K to $T = 350$ K. The estimated errors in our heat-capacity values vary from about $0.01 \cdot C_{p,m}$ at $T = 10$ K to $< 0.005 \cdot C_{p,m}$ at $T > 25$ K. The heat capacity of the sample represented about 0.53 to 0.84 of the measured total heat capacity. A plot of $C_{p,m}/R$ against T from 6 K to 350 K is presented in figure 1. The curve is smooth and without anomalies. It rises rapidly from $T \rightarrow 0$ to $T = 150$ K, above which the $C_{p,m}$ rises more slowly.

Special care was taken with respect to particle size and thermal history of our $(NH_4)_2PdCl_6$ sample in view of the hysteresis in $C_{p,m}$ encountered by other workers with various ammonium compounds, but not necessarily with ammonium hexachloropallidate. Reproducibilities of the heat-capacity of NH_4PF_6, $RbPF_6$, $(NH_4)_2SnCl_6$, K_2Cl_6, and Rb_2SnCl_6 were all dependent on particle size, which in turn was affected by thermal history.[27,28] In an n.m.r. study of KPF_6 and

TABLE 1. Experimental molar heat capacity of $(NH_4)_2PdCl_6$
($M = 355.2132\ g \cdot mol^{-1}$; $R = 8.31451\ J \cdot K^{-1} \cdot mol^{-1}$)

T/K	$C_{p,m}/R$	T/K	$C_{p,m}/R$	T/K	$C_{p,m}/R$	T/K	$C_{p,m}/R$	T/K	$C_{p,m}/R$
Series I		119.91	23.59	222.32	29.62	330.25	32.23	25.28	4.592
206.33	29.10	124.98	24.18	227.99	29.80	335.83	32.30	26.95	5.046
210.73	29.25	130.10	24.76	233.67	29.96	341.49	32.36	28.64	5.470
215.56	29.40	135.18	25.29	239.48	30.10	347.35	32.39	30.48	5.937
Series II		140.27	25.79	245.12	30.24	Series III		32.44	6.420
61.00	13.46	145.32	26.26	250.80	30.38	6.71	0.1571	34.44	6.910
66.79	14.74	150.51	26.69	256.49	30.52	7.78	0.2650	36.44	7.383
69.67	15.36	155.66	27.08	262.24	30.66	8.89	0.4007	38.44	7.852
72.89	16.02	160.30	27.39	267.91	30.80	10.08	0.5559	40.64	8.376
76.34	16.72	165.60	27.69	273.64	30.93	11.14	0.7290	43.01	8.966
79.24	17.27	171.31	27.99	279.25	31.06	12.27	0.9751	45.62	9.628
82.40	17.86	177.04	28.22	284.95	31.20	13.54	1.236	48.47	10.36
86.38	18.56	182.67	28.41	290.59	31.34	14.70	1.541	51.32	11.08
90.58	19.30	188.32	28.60	296.16	31.49	16.01	2.004	54.67	11.92
95.03	20.08	194.01	28.77	301.93	31.65	17.48	2.422	58.48	12.87
99.80	20.90	199.70	28.92	307.62	31.80	18.89	2.843	62.41	13.78
104.80	21.68	205.37	29.08	313.24	31.96	20.35	3.278	66.43	14.67
109.82	22.36	211.30	29.26	318.87	32.06	21.99	3.708	70.66	15.55
114.87	22.99	216.68	29.44	324.56	32.16	23.63	4.164	75.03	16.47

TABLE 2. Standard molar thermodynamic functions for $(NH_4)_2PdCl_6$
($M = 355.2132\ g \cdot mol^{-1}$; $p^\circ = 101.325\ kPa$; $R = 8.31451\ J \cdot K^{-1} \cdot mol^{-1}$; $\Phi_m^\circ \stackrel{def}{=} -\Delta_0^T H_m^\circ / T + \Delta_0^T S_m^\circ$

$\frac{T}{K}$	$\frac{C_{p,m}}{R}$	$\frac{\Delta_0^T S_m^\circ}{R}$	$\frac{\Delta_0^T H_m^\circ}{R \cdot K}$	$\frac{\Phi_m^\circ}{R}$	$\frac{T}{K}$	$\frac{C_{p,m}}{R}$	$\frac{\Delta_0^T S_m^\circ}{R}$	$\frac{\Delta_0^T H_m^\circ}{R \cdot K}$	$\frac{\Phi_m^\circ}{R}$
0	0	0	0	0	130	24.75	24.01	1729.0	10.71
5	(0.0665)	(0.0232)	(0.0883)	(0.0055)	135	25.27	24.95	1854.1	11.22
10	0.545	0.180	1.354	0.0443	140	25.77	25.88	1981.7	11.73
15	1.650	0.584	6.526	0.148	145	26.23	26.79	2111.7	12.23
20	3.150	1.264	18.58	0.335	150	26.65	27.69	2243.9	12.73
25	4.520	2.114	37.79	0.603	160	27.37	29.44	2514.1	13.72
30	5.820	3.054	63.66	0.932	170	27.92	31.11	2790.7	14.70
35	7.040	4.042	95.81	1.304	180	28.33	32.72	3072.1	15.65
40	8.220	5.058	134.0	1.709	190	28.65	34.26	3357.0	16.59
45	9.470	6.098	178.2	2.138	200	28.93	35.74	3644.9	17.51
50	10.74	7.161	228.7	2.587	210	29.22	37.16	3935.7	18.42
55	12.02	8.244	285.6	3.052	220	29.54	38.52	4229.5	19.30
60	13.23	9.342	348.7	3.530	230	29.84	39.84	4526.4	20.16
65	14.35	10.45	417.7	4.019	240	30.11	41.12	4826.1	21.01
70	15.43	11.55	492.2	4.518	250	30.36	42.35	5128.5	21.84
75	16.46	12.65	571.9	5.023	260	30.60	43.55	5433.3	22.65
80	17.41	13.74	656.5	5.534	270	30.85	44.71	5740.5	23.45
85	18.32	14.82	745.9	6.049	280	31.08	45.84	6050.2	24.23
90	19.19	15.90	839.7	6.566	290	31.33	46.93	6362.2	24.99
95	20.03	16.96	937.7	7.085	300	31.59	48.00	6676.8	25.74
100	20.94	18.0	1040.2	7.605	310	31.86	49.04	6994.1	26.48
105	21.71	19.0	1146.8	8.125	320	32.08	50.05	7313.8	27.20
110	22.40	20.0	1257.1	8.645	330	32.32	51.04	7635.4	27.90
115	23.01	21.0	1370.7	9.164	340	32.34	52.01	7958.3	28.60
120	23.60	22.0	1487.2	9.682	350	32.41	52.94	8282.0	29.28
125	24.19	23.05	1606.7	10.20	298.15	31.54	47.80	6618.4	25.60
						±0.05	±0.07	±10.0	±0.04

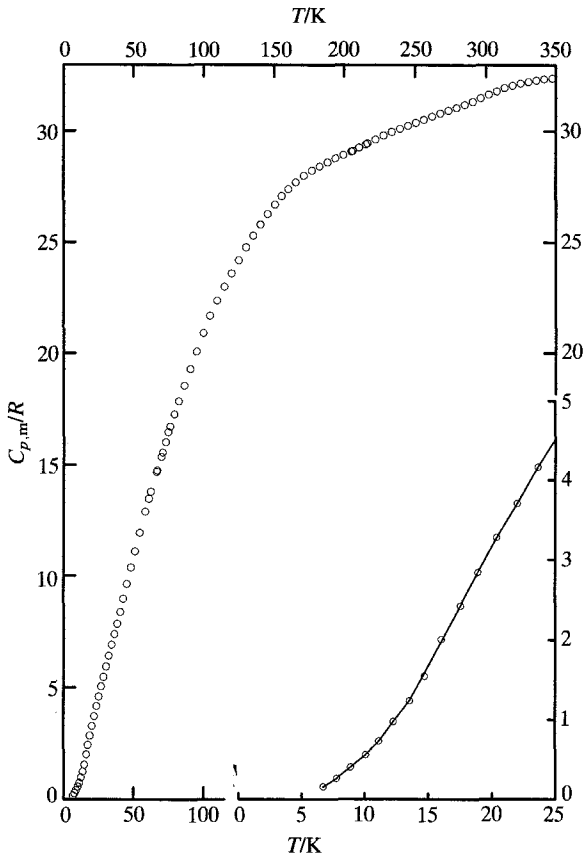

FIGURE 1. Experimental molar heat capacities $C_{p,m}$ at constant pressure plotted against temperature T for $(NH_4)_2PdCl_6$. The region $T < 25$ K is enlarged in the lower right-hand corner.

$RbPF_6$,[29] the temperature dependence of the fluorine resonance also depended on particle size and previous physical treatment. Reproducible results were obtained on samples in the form of fine powders. Those that were crystalline before their first cooling showed hysteresis and the process of cooling and warming broke up the crystallites into small particles, thereby eliminating the effects of hysteresis. Our sample of $(NH_4)_2PdCl_6$ was supplied as a finely divided powder. It was cooled to 206 K, and heat capacities were measured up to $T = 216$ K in Series I before the sample was cooled to 56 K. No hysteresis was apparent between the $C_{p,m}$ values determined in the overlap regions from Series I and II, and from Series II and III.

Integration of the smoothed values for heat capacity and enthalpy and entropy increments yielded the thermodynamic functions. Values of $C_{p,m}/R$ and the derived functions are presented at selected temperatures in table 2. The heat capacities below 6 K were obtained by fitting our experimental values below 20 K to the limiting form of the Debye equation with a plot of $C_{p,m}/T^3$ against T^2 extrapolated to $T \rightarrow 0$ (not

shown). Such a plot is also useful for identifying any non-vibrational contributions to the heat capacity at low temperatures. Although the quantity measured calorimetrically is $C_{\mathrm{sat,m}}$, it effectively equals $C_{p,\mathrm{m}}$ for these solids. The pressure effect of the helium exchange gas (0.3 kPa of helium at 20 K) on the heat capacity of solid $(NH_4)_2PdCl_6$, *i.e.* $(\partial C_{p,\mathrm{m}}/\partial p)_T$, is also negligible. In addition, the correction of $C_{p,\mathrm{m}}$ to $C_{V,\mathrm{m}}$, which is needed for analysis of any heat-capacity results, is negligible at these low temperatures so that the heat capacity of our $(NH_4)_2PdCl_6$ can be written as a power series:

$$C_{p,\mathrm{m}} = C_{V,\mathrm{m}} = aT^3 + bT^5 + cT^7 + \cdots. \tag{1}$$

The coefficients a, b, and c are directly related to the corresponding power series for the frequency spectrum at low frequencies.[30] Thus as $T \to 0$, the lattice heat capacity of the solid should become equal to that of an elastic continuum and, as such, can be described by the Debye "T^3" law:

$$C_{V,\mathrm{m}} = aT^3, \tag{2}$$

and

$$\Theta_0^c = (12\pi^4 Lk/5a)^{1/2}. \tag{3}$$

The Θ_0^c is the Debye characteristic temperature derived from heat capacities. From the plot of $C_{p,\mathrm{m}}/T^3$ against T^2 in the region $36 < (T^2/\mathrm{K}^2) < 400$, the experimental heat capacities for $(NH_4)_2PdCl_6$ follow a curve similar in shape to that for Ar and suggest that only lattice vibrations make significant contributions to the heat capacity in this temperature range. Extrapolation of the points below $T^2 = 36\ \mathrm{K}^2$ to cut the $T^2 = 0$ axis at a/R gives $10^4 \cdot a/R = (3.20 \pm 0.40) \cdot \mathrm{K}^{-3}$ or $10^4 \cdot a = (26.6 \pm 3.3)\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}}$, which yields from equation (3) $\Theta_0^c = (90.1 \pm 3.5)$ K. This compares with 93.5 K for Ar.

Only limited ancillary information is available to help interpret the motion of NH_4^+ within $(NH_4)_2PdCl_6$. The absence of λ-shaped or other anomalies in our heat-capacity results suggests that the $Fm\bar{3}m$ cubic structure is retained to $T = 6$ K, but crystallographic studies are unavailable to confirm this. The results of the measurements of the temperature dependence of the proton-spin relaxation times for polycrystalline $(NH_4)_2PdCl_6$ show that the NH_4^+ reorientation is the dominant relaxation mechanism above 56 K and the derived activation energy $\Delta^{\ddagger}U_{\mathrm{m}}^{\circ}$ for NH_4^+ lies between $211 \cdot R \cdot \mathrm{K}$,[31] and $307 \cdot R \cdot \mathrm{K}$.[12] Above 140 K, $PdCl_6^{2-}$ reorientation begins to contribute significantly to the relaxation time.[31] This picture parallels closely that of the NH_4^+ and $PtCl_6^{2-}$ in polycrystalline $(NH_4)_2PtCl_6$ where the $\Delta^{\ddagger}U_{\mathrm{m}}^{\circ}$ for NH_4^+ reorientation lies between $191 \cdot R \cdot \mathrm{K}$,[31] and $342 \cdot R \cdot \mathrm{K}$,[12] and the heat capacities vary smoothly with temperature without anomalies.[7] The calculated tunnelling frequencies for NH_4^+ in the salts of the family $(NH_4)_2MCl_6$ where M denotes Pd, Pt, Ir, Re, Sn, Pb, and Te, do not agree well with those measured experimentally.[1] The main reason for the discrepancy arises from the assumption in the model of three-fold sinusoidal potentials, whereas the actual potential is more boxlike near the minimum and the barrier is narrower. The discrepancies are greatest for the Pd and Pt salts whose barriers to NH_4^+ reorientation are the lowest.

We thank Dr R. D. Heyding for determining the crystal structure of our sample just prior to loading and Mrs J. Hale for help with the calculations. Two of us (J.E.C. and R.D.W.) acknowledge the Department of National Defence (Canada) for financial support.

REFERENCES

1. Prager, M.; Raaen, A. M.; Svare, I. *J. Phys. C: Solid State Phys.* **1983,** 16, L181.
2. Regelsberger, M.; Pelz, J. *Solid State Commun.* **1978,** 28, 783.
3. Morfee, R. G. S.; Staveley, L. A. K.; Walters, S. T.; Wigley, D. L. *J. Phys. Chem. Solids* **1960,** 13, 132.
4. Armstrong, R. L.; Mintz, D.; Powell, B. M.; Buyers, W. J. L. *Phys. Rev.* **1978,** B17, 1260.
5. Mintz, D.; Armstrong, R. L.; Powell, B. M.; Buyers, W. J. L. *Phys. Rev.* **1979,** B19, 448.
6. Callanan, J. E.; Weir, R. D.; Westrum, E. F., Jr. to be published.
7. Weir, R. D.; Westrum, E. F., Jr. *J. Chem. Thermodynamics* **1990,** 22, 1097.
8. Weir, R. D.; Westrum, E. F., Jr. *J. Chem. Thermodynamics* **1991,** 23, 653.
9. Callanan, J. E.; Weir, R. D.; Westrum, E. F., Jr. *J. Chem. Thermodynamics* **1992,** 24, 567.
10. Callanan, J. E.; Weir, R. D.; Westrum, E. F., Jr. *J. Chem. Thermodynamics* **1992,** 24, 661.
11. Kume, Y.; Miyazaki, Y.; Matsuo, T.; Suga, H.; David, W. I. F.; Ibberson, R. M. *Europhys. Lett.* **1991,** 16, 265.
12. Svare, I.; Raaen, A. M.; Thorkildsen, G. *J. Phys. C: Solid State Phys.* **1978,** 11, 4069.
13. Otnes, K.; Svare, I. *J. Phys. C: Solid State Phys.* **1979,** 12, 3899.
14. Smith, D. *J. Chem. Phys.* **1981,** 74, 6480.
15. Smith, D. *J. Chem. Phys.* **1985,** 82, 5133.
16. Hoser, A.; Prandtl, W.; Heger, G. *Proceedings ILL-IFF Workshop on Quantum Aspects of Molecular Motions in Solids.* Heidemann, A.; Magerl, A.; Prager, M.; Richler, D; Springer, T.: editors. Springer: Berlin. **1986,** pp. 19–23.
17. *Nat'l. Bur. Stand. (U.S.) Circ. No. 539,* **1955,** 5; see also Sharpe, A. G. *J. Chem. Soc.* **1953,** 4177.
18. Westrum, E. F., Jr; Furukawa, G. T.; McCullough, J. P. *Experimental Thermodynamics, Vol. 1.* McCullough, J. P.; Scott, D. W.: editors. Butterworths: London. **1968,** p. 133.
19. Stimson, H. F. *J. Res. Natl. Bur. Stand. (U.S.)* **1961,** 65A, 139.
20. McCrackin, F. L.; Chang, S. S. *Rev. Sci. Instrum.* **1975,** 46, 550.
21. Chirico, R. D.; Westrum, E. F., Jr. *J. Chem. Thermodynamics* **1980,** 12, 311.
22. Goldberg, R. N.; Weir, R. D. *Pure Appl. Chem.* **1922,** 64 (in press).
23. Bedford, R. E.; Durieux, M.; Muijlwijk, R.; Barber, C. R. *Metrologia* **1969,** 5, 47.
24. Westrum, E. F., Jr. *Proceedings NATO Advanced Study Institute on Thermochemistry, Viana do Castello, Portugal.* Ribeiro da Silva, M. A. V.: editor. Reidel: New York. **1984,** p. 745.
25. Andrews, J. T. S.; Norton, P. A.; Westrum, E. F., Jr. *J. Chem. Thermodynamics* **1978,** 10, 949.
26. *Pure Appl. Chem.* **1986,** 58, 1678.
27. Staveley, L. A. K.; Grey, N. R.; Layzell, M. J. *Z. Naturforsch.* **1963,** 18A, 148.
28. Morphee, R. G. S.; Staveley, L. A. K. *Nature* **1957,** 180, 1246.
29. Miller, G. R.; Gutowsky, H. S. *J. Chem. Phys.* **1963,** 39, 1983.
30. Barron, T. H. K.; Berg, W. T.; Morrison, J. A. *Proc. Roy. Soc. London* **1957,** A242, 478.
31. Bonari, M.; Terenzi, M. *Chem. Phys. Lett.* **1974,** 27, 281.