presence of SO. It seems clear that there is no incontrovertible data to support the existence of S_2O_2.

The salient feature which has led the majority of workers to believe in the presence of SO in the discharge product is the apparent 1:1 sulfur to oxygen ratio. It was only in his later work that Schenk was able to construct a reliable manometer and observe the anomalous 25% pressure decrease upon decomposition into sulfur and SO_2. In order to explain this apparent stoichiometery it would seem reasonable to assume that SO emerges from the discharge tube and polymerizes according to

$$3SO = S_2O + SO_2 \qquad (5)$$

However, from their observation of a negligible pressure change in the discharge products, Evans, Scott and Huston[9] have established that such a polymerization must occur in a period of less than 3 seconds after leaving the discharge tube. In another experiment[10] an attempt was made to observe the ultraviolet absorption due to SO in the products which were rapidly pumped out of a discharge tube. No SO absorption could be detected. However, from the recent work of St. Pierre and Chipman[11] it is now definitely known that SO is stable in a sulfur-rich system near 1,000°. So that if one considers a discharge tube and a low pressure flame to have a high effective temperature then it is reasonable to consider SO as the primary discharge product, despite the fact that there is no direct evidence for it.

It should be pointed out that in a few cases (see Table I of reference 9 and Table II of this paper) a product is obtained which is apparently definitely over 50% in S_2O. This can be interpreted as due to the reaction

$$SO + S_x = S_2O + S_{x-1} \qquad (6)$$

It would also be possible that in the discharge oxygen atoms could be considered as the primary discharge product. In this case both SO and S_2O could result from the capture of oxygen atoms by sulfur molecules much as ozone is formed in the pure oxygen system. If this were the case then the apparent 1:1 sulfur to oxygen ratio would only be a coincidence of kinetic factors.

A third possibility rests on the unknown thermodynamic stability of S_2O. It is clear that S_2O is unstable at room temperature and at temperatures only slightly above room temperature. It is possible, however, that S_2O may be a stable species at elevated temperatures. In either case the thermodynamic stability of S_2O should be investigated and its importance in the sulfur–oxygen system established.

Acknowledgments.–We are indebted to Dr. D. P. Stevenson of the Shell Development Company for making possible the mass spectrographic analysis. One of the authors (D.J.M.) also wishes to acknowledge financial support from the Allied Chemical and Dye Corporation and the National Science Foundation.

BERKELEY 4, CALIF.

---

[9] E. Evans, A. Scott and J. Huston, THIS JOURNAL, **74**, 5525 (1952).

[10] Unpublished experiments by E. Becker.

[11] G. St. Pierre and J. Chipman, THIS JOURNAL, **76**, 4787 (1954).

[CONTRIBUTION NO. 86 FROM THE CRYOGENIC LABORATORY OF THE PENNSYLVANIA STATE UNIVERSITY]

Heat Capacity and Magnetic Susceptibility of Vanadium(III) Ammonium Alum from 1.1 to 20°K.

BY J. J. FRITZ AND H. L. PINCH[1]

RECEIVED JUNE 25, 1956

The heat capacity and magnetic susceptibility of vanadium(III) ammonium alum have been measured (in zero magnetic field) from 1.1 to 20°K. The heat capacities show a distinct Schottky transition. This is explained by the assumption that the lowest set of energy levels of the vanadium ion are a singlet and a doublet, with a separation of 4.9 cm.$^{-1}$. The magnetic susceptibilities are substantially in accord with previous less extensive measurements.

Introduction

The magnetic behavior at low temperatures of vanadium(III) ammonium alum is distinctly different from that of the paramagnetic alums of chromium, iron and titanium(III). Despite the fact that vanadium alum possesses the high crystalline symmetry and great magnetic dilution characteristic of the alum structure, it shows large deviations from ideal behavior. The theoretical reasons for this behavior have been discussed by Siegert[2] and Van Vleck.[3]

The theoretical treatment assumes substantial "quenching" of the orbital magnetic moment due to the $^3F_2$ ground state. As a result, the state is split into seven (2L + 1) orbital states (largely degenerate), each of which is further split into three spin states (a singlet and a doublet separated by an amount δ). The over-all orbital splitting is assigned as about 10^4 cm.$^{-1}$. At low temperatures the only orbital states of consequence are the three lowest; the theory assigns these as a singlet and a doublet with a spacing (Δ) of about 10^3 cm.$^{-1}$.

Siegert[2] analyzed the magnetic susceptibility measurements of Van den Handel and Siegert[4] and concluded that the splitting, δ, between spin levels was about 5 cm.$^{-1}$. The magnitude assigned to the orbital splitting, Δ, depended considerably on the details of the theory.

The heat capacity of the salt below 20°K. provides a direct check on the validity of the assignment of

---

[1] Abstracted in part from the Ph.D. thesis of H. L. Pinch.

[2] A. Siegert, *Physica*, **3**, 85 (1936); **4**, 138 (1937).

[3] J. H. Van Vleck, *J. Chem. Phys.*, **7**, 61 (1939).

[4] J. D. Van den Handel and A. Siegert, *Physica*, **4**, 871 (1937).

spin levels. The heat capacity was determined in the present research, and in addition the magnetic susceptibility of the salt was investigated further.

Experimental

The general experimental arrangement was similar to that of Fritz and Giauque.[5] The chief differences were: (1) separate glass Dewar vessels were used for liquid nitrogen and liquid helium; the latter was arranged so that it and the apparatus within it were both removable and transportable. (2) The level of liquid helium (or other refrigerant) was measured by use of a set of four $^1/_2$-watt carbon resistors spaced at approximately equal intervals from top to bottom of the helium Dewar. (3) A series of thin brass baffles in the upper part of the helium Dewar served to block radiation from the top and to promote heat transfer to escaping helium vapor.

The glass sample container was blown in the shape of an ellipsoid of revolution with interior semi-major axis of 5.97 cm. and semi-minor axis of 1.245 cm. Its internal volume was 37.54 cm.^{3} This was about 3% less than that calculated from axial dimensions, due mainly to rounding at the ends; at other points the interior dimensions matched those calculated within 0.5 mm. A conical "cooling chamber" of 1.5 cm.^{3} volume was sealed to the top of the sample container. The weight of the container was 34.51 g.

The thermometer-heater on the outside of the sample container was of Molacco Black (Binney and Smith Company), painted on paper as described by Giauque, Stout and Clark.[6] It had a resistance at room temperature of about 2000 ohms. This thermometer possessed remarkable stability; its behavior is discussed briefly below. Vacuum jacketing of the specimen and electrical connections to the thermometer were accomplished as previously described.[5]

Measurements of the electrical resistance of the thermometer were made potentiometrically. The thermometer was calibrated against vapor pressures of hydrogen and helium. During energy input, the heating current was measured by means of a calibrated micro-ammeter; the heating voltage was determined before and after each heating period by measurement of the current it developed in a calibrated resistance box. Each energy input was corrected for all heat developed in external leads and for half of that produced inside the vacuum jacket of the calorimeter.

Measurements of magnetic susceptibility were made by means of a set of coils similar to that described by Giauque, Fritz and Lyon,[7] as "secondary fluxmeter coils." These were in turn calibrated against an external set of coils like that described by Giauque, *et al.*, as "primary fluxmeter coils," but considerably more compact.

In the preparation of the specimen used, C.P. anhydrous V_2O_5 was first converted into ammonium meta-vanadate by the procedures of "Inorganic Syntheses."[8] The alum was produced, as described by Grobitch,[9] by an initial reduction of the meta-vanadate with SO_2 to ammonium vanadyl sulfate followed by electrolytic reduction in dilute sulfuric acid to vanadium(III) sulfate. The alum was then crystallized by cooling of the solution. A portion of the alum was analyzed for total vanadium, sulfate and ammonium, with water obtained by difference.

The crystals, originally 0.1 to 1 cm. long, were ground to a 60-mesh powder in a nitrogen atmosphere. Final grinding was done at or below 0° to minimize dehydration, and the sample used was stored for several hours under moist nitrogen gas before being put into the ellipsoidal container. Despite all precautions, the final specimen contained 2.5% of the vanadium in the tetravalent state. The water content was 99.2% of the theoretical value for the alum based on the vanadium content. The specimen used weighed 43.944 g. and contained 0.09276 mole of total vanadium. After the sample container had been filled with the salt, the gas space within it was filled to 1 atm. with a gas mixture containing 94 mole % nitrogen, 6 mole % helium; the container was then sealed off.

Results

Measurements of the heat capacity of the alum were made in two separate experiments. The first (series I) extended from 1.8 to 21.8°K.; the second (series II) only from 1.2 to 2.1°K. The observed heat capacities were corrected for the heat capacity of 34.51 g. of Pyrex by use of the formula Cp(Pyrex) = $1.07 \times 10^{-4}T^3$ cal. deg.$^{-1}$ g.$^{-1}$, obtained from the data of Lyon and Giauque.[10] Above 10°K., this correction amounted to about $^1/_3$ of the total heat capacity. The values of the heat capacity per mole of total vanadium are given in Table I. The uncertainty in the individual points is estimated to be about 1%; in general, the points fit a smooth curve to somewhat better than a per cent.

The separation of the heat capacity into "magnetic" and "lattice" contributions was done by successive approximations. In this process the magnetic heat capacity above 5°K. was represented by a Schottky-type function, and the lattice contribution below 5° by a T^3 law.

Three series of measurements of magnetic susceptibility were made over a six-month period. Although the constants of the coils changed somewhat between series, deviations of the results were random and at most 4%. The accuracy of susceptibility measurements is estimated as 3%.

The molal magnetic susceptibilities are plotted against T in Fig. 1. The circles represent values obtained in this research, and the heavy line is drawn through the experimental points. The triangles are the results of Van den Handel and Siegert,[4] and the broken line is their theoretical curve. It will be seen that the two sets of data are in substantial agreement except in the region between 3 and 6°K. The data above 3°K. can be represented approximately by the equation $\chi_M = 0.97/(T + 2.1)$. Below 3°K. the susceptibility approaches a constant value, and must be represented by a more complex relationship, such as that of Van den Handel and Siegert.[4]

An adiabatic magnetization made at 3.3°K. indicated a warming of less than 0.02°K. upon application of 7000 gauss.

Discussion

The heat capacity data indicate clearly the existence of a Schottky-type transition in the liquid helium range. We have assumed, as did Siegert[2] and Van Vleck,[3] that the three lowest magnetic states ("spin states") consist of a singlet ground level and a doublet upper level. On this basis, the separation between the two energy levels is 4.9 cm.$^{-1}$, in good agreement with the value of 4.8 cm.$^{-1}$ estimated by Van den Handel and Siegert.[4]

The maximum in the magnetic heat capacity is 1.46 cal. mole^{-1} deg.$^{-1}$, compared with the value of 1.51 calculated from the model above. This difference has been arbitrarily assigned to failure of the 2.5% tetravalent vanadium present to take part in the magnetic transition. A Schottky curve based on 0.975 mole of trivalent vanadium fits the

---

(5) J. J. Fritz and W. F. Giauque, THIS JOURNAL, **71**, 2168 (1948).

(6) W. F. Giauque, J. W. Stout and C. W. Clark, *ibid.*, **60**, 1053 (1938).

(7) W. F. Giauque, J. J. Fritz and D. N. Lyon, *ibid.*, **71**, 1657 (1949).

(8) "Inorganic Syntheses," Vol. 3, McGraw-Hill Book Co., Inc., New York, N. Y., 1950, p. 117.

(9) H. Grobitch, "Inorganisch-Präparative Chimie," Springer, Vienna, 1950, p. 416.

(10) D. N. Lyon and W. F. Giauque, THIS JOURNAL, **71**, 1647 (1949).

TABLE I

HEAT CAPACITY OF VANADIUM AMMONIUM ALUM, CAL. MOLE^{-1} DEG.$^{-1}$

Temp., °K.	C_p (obsd.)	C_p (magnetic)	C_p (lattice)
	Series I		
1.808	1.111	1.107	0.004
2.244	1.379	1.371	.008
2.440	1.412	1.402	.010
2.630	1.459	1.446	.013
2.832	1.467	1.451	.016
3.332	1.363	1.334	.029
3.570	1.317	1.285	.032
4.007	1.196	1.151	.045
4.564	1.018	0.952	.066
5.104	0.921	.828	.093
5.68	.815	.669	.146
6.30	.756	.560	.196
6.88	.746	.480	.266
7.57	.780	.407	.373
8.15	.844	.346	.498
8.75	.909	.308	.601
9.46	1.032	.270	.762
10.29	1.215	.227	.988
11.40	1.464	.179	1.285
11.91	1.588	.165	1.423
12.86	1.849	.140	1.709
14.07	2.374	.117	2.257
14.54	2.408	.111	2.30
15.77	3.02	.09	2.93
17.72	4.31	.07	4.24
19.73	5.87	.06	5.87
21.66	6.65	.05	6.60
	Series II		
1.308	0.611	0.609	0.002
1.448	.747	.745	.002
1.627	.931	.928	.003
1.832	1.105	1.101	.004
2.023	1.248	1.242	.006

magnetic heat capacity within 2% below 4°K., except for the lowest point. The equation used was $C/R = 1.95\,(\delta/kT)^2e^{-\delta/kT}(1 - 2e^{-\delta/kT}) - 2$, with $\delta =$ 4.9 cm.$^{-1}$, so that $\delta/k = 7.1°$. This curve has been used for estimation of the magnetic heat capacity above 6°K.

The magnetic contribution to the entropy has been calculated using the Schottky curve for extrapolation below 1°K. and above 6°K. (these contributed 0.09 and 0.33 e.u., respectively). The total magnetic entropy of the salt was 2.135 ± 0.01 cal. mole^{-1} deg.$^{-1}$; the theoretical value for 0.975 mole of salt with R ln 3 per mole is 2.129 cal. mole^{-1} deg.$^{-1}$. The total entropy per mole of vanadium is 3.05 cal. mole^{-1} deg.$^{-1}$ at 15°K. and 4.24 cal. mole^{-1} deg.$^{-1}$ at 20°K.

The assumptions made by Siegert[2] in theoretical treatment of the magnetic susceptibilities have been questioned (for example, see ref. 3). Except for the region 4 to 6°, our measurements are in agreement with the less extensive measurements of Van den Handel and Siegert.[4] The region of disagreement does not lend itself to any obvious improvement in the theory.

The very small heating on adiabatic magnetization at 3.3 °K. was consistent with that calculated from the heat capacity and susceptibility of the salt. In view of the small effect of the field, no further magnetizations were made.

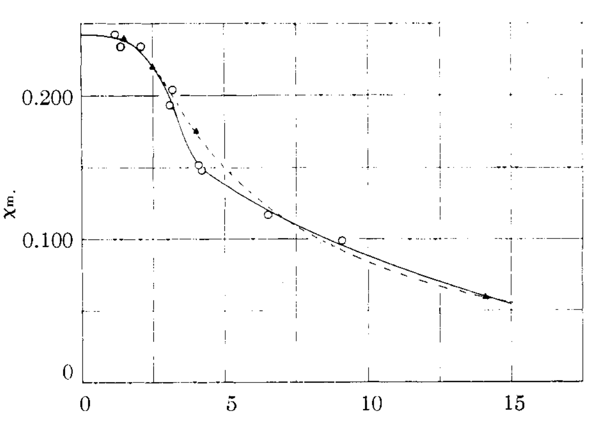

Fig. 1.—Magnetic susceptibility of vanadium ammonium alum.

The lattice heat capacity fits the equation $C_p = 7.5 \times 10^{-4}T^3$ cal. mole^{-1} deg.$^{-1}$ within 1% between 14 and 20°K. Below 14° the constant in the T^3 expression rises gradually, reaching 9×10^{-4} at 9°K., and then drops back. The increase in the constant is definitely beyond experimental error. A similar behavior, but more pronounced, was observed by Duyckaerts[11] for ferric ammonium alum between 8 and 20°K. The lattice heat capacity of vanadium alum between 15 and 20°K. is approximately the same as that obtained for potassium chromium alum by Johnston.[12] It is about 20% less than that given for ferric ammonium alum by Duyckaerts.[11]

Stability of the Carbon Thermometer.—The carbon thermometer heater proved remarkably stable. After its first cooling to 20°K., the room temperature resistance (about 2050 ohms) changed by 20 ohms. Thereafter it changed by only two ohms over a six-month period, despite repeated cycles of cooling and warming. For a given low temperature, the ratio $R_T/R_{300°}$ was constant within about 0.1% (2–3 ohms) for all measurements. At 4°K., this variation corresponded to about 0.02°. It would thus appear that after an initial full calibration at low temperatures, it would have been possible to base a temperature scale, within 0.02°, upon a measurement of room temperature resistance alone. It would appear almost certain that temperatures in the helium range could thereafter have been based on a calibration at 4.2°K. alone, within the accuracy of the initial calibration.

Acknowledgments.—We wish to thank Prof. J. G. Aston for helpful discussions, Mr. Leslie F. Shultz for production of refrigerants, and the National Science Foundation for support in the latter stages of the experiments. We gratefully acknowledge the provision of funds for the iron-free solenoid magnet by the Research Corporation and the Westinghouse Electric Company.

UNIVERSITY PARK, PA.

---

[11] G. Duyckaerts, *Mem. Soc. Roy. Sci. Liege*, **6**, 195 (1943).

[12] H. L. Johnston, J. Hu and W. S. Horton, THIS JOURNAL, **75**, 3922 (1953).