

Fig. 3.—Cell dimensions versus composition for $(\text{Ba}_{1-x}\text{Sr}_x)\text{Ta}_4\text{O}_{15}$.

those of pure $\text{Ba}_5\text{Ta}_4\text{O}_{15}$. Since Sr was present, it was assumed that the product was $(\text{Ba}_{1-x}\text{Sr}_x)_5\text{Ta}_4\text{O}_{15}$. To test this possibility $\text{Sr}_5\text{Ta}_4\text{O}_{15}$ was prepared, and attempts were made to obtain solid solutions of $\text{Ba}_5\text{Ta}_4\text{O}_{15}$ and $\text{Sr}_5\text{Ta}_4\text{O}_{15}$.

These attempts were successful. Figure 3 shows plots of cell dimensions versus composition for this series. The cell size for the end product of the $\text{Ba}_5\text{SrTa}_2\text{O}_9$ conversion corresponded to the composition $(\text{Ba}_{0.85}\text{Sr}_{0.15})_5\text{Ta}_4\text{O}_{15}$. No theoretical significance is attached to the straight lines drawn through the points. A smooth curve could have been used to indicate a continuous change in cell dimensions.

Conclusion

Of the various divalent cations substituted in the octahedrally coordinated positions, all except Sr^{II} , the largest ion of the series, substituted for tantalum in a random way. This result is consistent with the general observation that large size difference, as well as large charge difference, leads to ordered arrangements. In the perovskite-like compounds $\text{Ba}_2\text{M}^{IV}\text{W}^{VI}\text{O}_6$, ordering was observed regularly.⁴ In the $\text{Ba}_3\text{M}^{IV}\text{Ta}_2\text{O}_9$ series, on the other hand, the smaller charge difference (+2 vs. +5) leads to ordering only when combined with the large size of Sr^{II} .

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Magnetic and Thermodynamic Properties of Potassium Ferricyanide at Low Temperatures

BY L. V. GREGOR¹ AND J. J. FRITZ

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The heat capacity and magnetic susceptibility of potassium ferricyanide have been measured from 0.6° to 20°K. There is a small peak in the heat capacity below 2°K. whose maximum is at 1.2°, and $\chi_m T$ decreases sharply below 2°. The susceptibility obeys a Curie-Weiss law between 20° and 2°K. The entropy removed by isothermal magnetization to 7040 oersteds at 1.245°K. was 0.122 e.u. Adiabatic demagnetization from this point lowered the temperature to 0.52°K.

Introduction

This paper reports the latest in a series of investigations by this Laboratory of the magnetic and thermodynamic properties of compounds involving the first transition series (iron group) elements. Previous studies²⁻⁴ have reported a variety of effects due to interactions of the magnetic ions with surrounding ions and molecules. These interactions usually result in deviations of the magnetic susceptibility from Curie or Curie-Weiss law behavior and in heat capacity anomalies at low temperatures.

In potassium ferricyanide, the $\text{Fe}(\text{CN})_6^{-3}$ ion is an octahedral complex. Two of the five 3d orbitals of the ferric ion are used in the $d\gamma^2sp^3$ bonding orbitals, leaving three d_e orbitals for the five remaining electrons. Two electrons each are paired in two d_e orbitals, leaving a single unpaired

electron. The magnetic susceptibility accordingly is much closer to that corresponding to a single unpaired electron than to that of the normal $^6S_{5/2}$ ground state of Fe^{+3} . Although the crystal structure of $\text{K}_3\text{Fe}(\text{CN})_6$, space group $C_{2h}^5-P2_1/c$, is monoclinic, the angle between the c -axis and the plane of the a - and b -axis is $90^\circ 6'$, so that the structure is pseudo-orthorhombic.⁵ Crystal structure data indicate that there are two non-equivalent ferricyanide ions per unit cell.⁶

The principal susceptibilities of $\text{K}_3\text{Fe}(\text{CN})_6$ were measured by Jackson⁷ from 14° to 290°K. The susceptibility is distinctly anisotropic, and for the powdered salt is twice the amount expected for a single unpaired electron. At 14°K. the powder susceptibility is close to the value for a single unpaired electron. The anisotropy observed by Jackson was explained by Howard⁸ in terms of a rhombic, almost axial, crystal field acting on the d_e orbitals. Howard's treatment succeeded in re-

(1) Department of Chemistry, University of California, Berkeley 4, California.

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producing the observed anisotropy but gave only moderate agreement with the observed susceptibilities.

More recently, McKim and Wolf⁹ have extended the measurements of the principal susceptibilities down to 1°K. and in addition Baker, Bleaney and Bowers¹⁰ have measured the microwave absorption of both $K_3Fe(CN)_6$ and a specimen in which the salt was diluted with the diamagnetic isomorph $K_3Co(CN)_6$. They found it possible to explain the results obtained with the diluted salt using the theoretical treatment of Bleaney and O'Brien¹¹ which combined a crystal field of general symmetry with the addition of a factor to account for π binding between the iron atom and the (CN) ligands. Only general agreement was obtained with the rather diffuse results for the concentrated salt. Agreement with susceptibility data was again only fair. Baker, Bleaney and Bowers¹⁰ suggest that there is probably considerable exchange between neighboring ferricyanide groups.

The heat capacity of $K_3Fe(CN)_6$ has been measured from 15° to 298° by Stephenson and Morrow,¹² who found a broad shallow anomaly between 50° and 160°K. This anomaly is by no means large enough to account for the $R \ln 2$ entropy associated with the doubly-degenerate ground state due to the spin of the single unpaired electron and may not even be associated with magnetic phenomena.

The bonding of nitrogen directly to the metal ion appears to enhance and complicate magnetic interactions in transition-metal complexes; we have observed this quite strikingly in Cu(II) compounds.^{2,3} In view of the rather ambiguous state of affairs with regard to $K_3Fe(CN)_6$, we have taken advantage of the opportunity to increase the available evidence by a detailed examination of the heat capacity and magnetic behavior of this salt at low temperatures.

Experimental

Reagent grade $K_3Fe(CN)_6$ was recrystallized and dried in accordance with procedures for primary standard reagents. As a check, an iodine-thiosulfate titration showed that the percentage of Fe^{+3} in the sample was within 0.05% of the theoretical value. The sample was ground to a fine powder and packed tightly into an ellipsoidal Pyrex bulb 31.13 cm.³ in volume. The sample weighed 34.01 g. (0.1033 gram ion Fe^{+3}). The sample was evacuated to 10^{-6} mm. for 11 hr. at room temperature to remove water and adsorbed gases. The bulb was filled with a dry helium-nitrogen mixture to a pressure of 1 atmosphere and sealed off. The amount of glass in thermal equilibrium with the sample was 16.21 g.

A carbon thermometer-heater¹³ was placed around the outside of the sample container as described previously.² The thermometer was initially calibrated at 10 points in the hydrogen and helium range; the resistance was a smooth but non-linear function of $\log T$. These data were used to construct a standard temperature scale with smooth first and second derivatives. The thermometer was more sensitive but not as stable from one set of measurements to the

next as those previously described.² Several calibration points were obtained during each set of measurements; the factors necessary for correction of observed resistances to the standard scale were determined by comparison of resistances at these calibration points. The effect of the magnetic field H on the thermometer resistance R , determined at 4°, 20° and 77°K., fitted the equation

$$R_0 = R + a \left(\frac{H}{T} \right)^2 \quad (1)$$

This equation was used for interpretation of resistances measured in a magnetic field.

The initial molar magnetic susceptibility χ_0 was measured with the fluxmeter described previously.^{2,4} The average susceptibility of $K_3Fe(CN)_6$ at 77°K.⁷ was used to obtain the fluxmeter coil constant (*i.e.*, turn-area of sample coils in the absence of sample, corrected for diamagnetism). Susceptibility measurements in magnetic fields (and also in zero field) were made at 400 cycles/sec. with the modified General Radio Co. inductance bridge as before.⁴ These measurements were corrected for the effect of the magnetic field of the measuring coils and for the slow drift with time of the geometric inductance of the coils.⁴ Magnetic fields up to 7050 oersteds were obtained with the iron-free solenoid magnet previously described.¹

Heat capacity measurements were made in the manner previously described.¹ Above 12°K., the change of temperature with time after heating were non-linear. This was attributed to imperfect heat transfer between the superheated thermometer and the sample during this period. Correction was made for these non-linear temperature drifts by a method similar to that developed by Keesom and Kok and modified by Aston and Szasz.¹⁴ The details of the treatment are given elsewhere.¹⁵

Results

Heat capacities were measured from 0.6° to 21°K. in two overlapping series. The data are given in Table I. Figure 1 illustrates the data

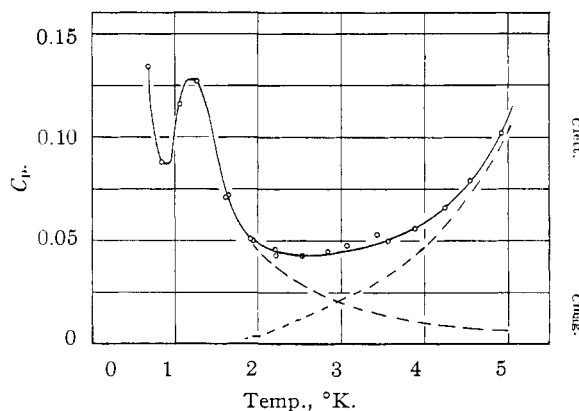


Fig. 1.—Heat capacity of $K_3Fe(CN)_6$ below 5°K.

below 5°K. The uncertainty in an individual measurement below 12° is estimated at 1%, but the data follow a smooth curve much better than this. Above 12°, the maximum deviation from the smooth curve is 3%, probably because of the corrections for non-linear afterdrifts and for the heat capacity of the Pyrex glass in contact with sample. The latter correction was made by using the data of Giaque and Lyon for the heat capacity of Pyrex.¹⁶ The probable error in this range is

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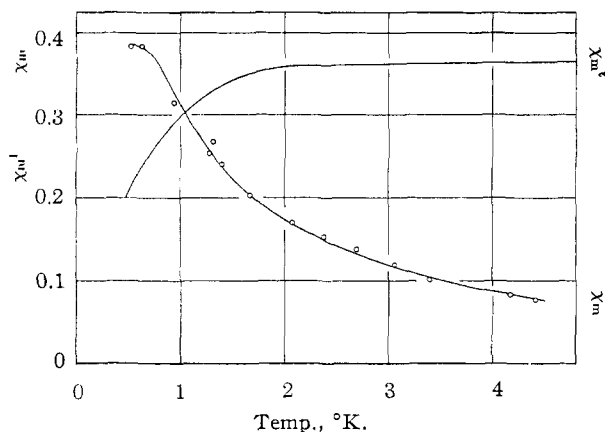


Fig. 2.—Molar magnetic susceptibility of $K_3Fe(CN)_6$ below $5^\circ K$.

estimated as 3%. Above 15° , the data agree well with those of previous investigations.⁷ The value at $1.05^\circ K$. is about 50% larger than that estimated by McKim and Wolf.⁹

In the low-temperature region, there is a small but definite peak in the heat capacity curve with its maximum at 1.15° . There are indications of a possible second peak at or below $0.6^\circ K$. The lattice heat capacity is given by the equation

$$C_l = \alpha T^3 \quad (2)$$

where the "constant" α rises linearly with decreasing temperature from 5.9×10^{-4} at 20° to 9.0×10^{-4} at 8° and then levels off. When the lattice heat capacity calculated from the equation above is subtracted from the total, the remaining "magnetic" heat capacity above 1.2° is given by the expression

$$C_{(mag)} = \frac{0.18}{T^2} \quad (3)$$

In Fig. 1, $C_{(mag)}$ and C_l are shown as broken lines.

The magnetic susceptibility in zero magnetic field was measured with the fluxmeter at 31 points between 0.52 and $20.2^\circ K$. The precision of the observations was about 0.001 unit in the molar magnetic susceptibility (χ_m); the accuracy is estimated as 1% for susceptibilities greater than 0.1. Above $4^\circ K$. the data can be represented within experimental precision by a Curie-Weiss Law

$$\chi_m = \frac{0.368}{T + 0.14} \quad (4)$$

Below 2° , $\chi_m T$ falls off rapidly, and the susceptibility approaches a maximum at about $0.7^\circ K$. The behavior below 5° is shown in Fig. 2. The actual points are shown for the susceptibility, χ_m ; a smoothed curve is drawn in for the product $\chi_m T$.

The estimation of the thermodynamic temperatures below $1^\circ K$. required knowledge of the intensity of magnetization I as a function of H and T , obtained by use of the adiabatic susceptibility $(\partial I / \partial H)_S$ measured along the isentropes obtained in the several adiabatic magnetizations. These susceptibilities were obtained with the inductance bridge at 400 cycles. Before employing them in further calculation, it was necessary to determine

TABLE I
HEAT CAPACITY OF POTASSIUM FERRICYANIDE

Temp., °K.	C_p , cal./mole deg.	Temp., °K.	C_p , cal./mole deg.	Temp., °K.	C_p , cal./mole deg.
0.67	0.134	3.910	0.056	12.54	1.53
0.84	.088	4.245	.066	12.65	1.77
1.06	.116	4.544	.079	13.46	1.85
1.283	.127	4.92	.102	14.23	2.27
1.614	.071	5.36	.134	14.27	2.14
1.628	.072	5.88	.185	15.02	2.5
1.905	.051	6.28	.238	15.38	2.7
1.942	.050	6.70	.283	15.78	2.9
2.204	.046	7.24	.374	16.06	2.7
2.213	.043	7.89	.443	16.37	2.9
2.535	.043	8.61	.566	17.04	3.4
2.844	.045	9.48	.704	17.09	3.2
3.074	.048	10.40	.870	18.15	3.5
3.437	.053	11.44	1.11	18.40	3.8
3.570	.050	11.84	1.35	19.90	4.7

whether there was any dependence of susceptibility on frequency in the range of temperature studied. Preliminary evidence on this point was given by the fact that intercomparison of bridge and fluxmeter readings at twelve points in the helium range were all consistent within the accuracy of the bridge observations. A more rigorous test of the lack of dependence of susceptibility on frequency (up to 400 cycles) was obtained in connection with the magnetizations themselves. During these experiments a 400-cycle field of about 10 gauss was imposed on the specimen itself for 20 to 30 minutes. In no case was there any detectable absorption of energy due to the alternating magnetic field, indicating that the imaginary component (χ'') of the susceptibility at 400 cycles must be less than 0.1% of the real component (χ') and thus that the susceptibility observed at 400 cycles must be the same as that at zero frequency.

The intensity of magnetization, I , in the magnetic field at temperatures above $1.25^\circ K$. was calculated by integration of the data of the four adiabatic magnetizations. The values obtained from 11 points fitted the equation

$$I = 0.346 \left(\frac{H}{T} \right) - 8.0 \times 10^{-8} \left(\frac{H}{T} \right)^2 \quad (5)$$

for values of H/T from 500 to 5,000 oersteds/degree. This equation for I then was used to obtain entropies of magnetization at $1.25^\circ K$. which were then used, in conjunction with the heat capacity measurements and isentropic magnetizations starting below $1.25^\circ K$., to calculate thermodynamic temperatures by standard methods.⁴ Because of the limited amount of data, the entropy change accompanying each of the heat capacity determinations was divided into the corresponding enthalpy change to obtain the average temperature, which was then associated with the average resistance of the thermometer. Three points were obtained in this fashion, making possible a smooth extension of the resistance temperature scale to $0.5^\circ K$. The lowest temperature actually attained, by demagnetization from 7050 oersteds at 1.248° , was $0.52^\circ K$.; the entropy removed in the magnetization was 0.122 e.u.,

about 9% of the entropy expected for a doubly-degenerate ground state.

Discussion

The heat capacity anomaly and the corresponding decrease in $\chi_m T$ below 2°K. suggest that a cooperative or "exchange" interaction between the magnetic ions becomes important at these temperatures. Such an interaction had previously been deduced from the paramagnetic resonance spectrum of $K_3Fe(CN)_6$ at low temperatures.¹¹ The heat capacity anomaly is much too small to account for the $R \ln 2$ magnetic entropy of the spin doublet ground state at high temperatures. The high heat capacity observed by Stephenson and Morrow between 50° and 160°K. was attributed to magnetic interactions, who estimated the entropy associated with this anomaly as 0.09 ± 0.02 e.u.¹² It does not appear that their anomaly is due to removal of the spin degeneracy, since even below 20°K. $K_3Fe(CN)_6$ still possesses a magnetic susceptibility nearly the same as that expected for a single unpaired electron. The "high-temperature" anomaly may be associated with a "quenching" of the orbital magnetic moment, which contributes significantly to the susceptibility at higher temperatures and may be appreciable even at 20°, according to the calculations of Howard.⁸ Whatever the cause, it is evident that even the sum of the entropy decreases associated with the two regions of high heat capacity is insufficient to account for all the magnetic entropy. It seems likely that there is a peak in the heat capacity below 0.6°, the beginning of which may be the observed rise in the heat capacity curve at 0.75°.

Both the heat capacity and the magnetic susceptibility indicate that there are pronounced interactions between the magnetic ion and its surroundings. In the first place, the observed structure of the heat capacity curve and the hint of additional structure below 0.7°K. indicate the presence of fairly complicated cooperative effects. Second, the fact that no dispersion effects were

observed in the 400 cycle susceptibility indicates that any relaxation time present is substantially below a millisecond even below 1°K. This is in marked contrast to the behavior of such salts as the paramagnetic alums, whose relaxation times are typically above 0.01 second at liquid helium temperatures.¹⁷ The existence of cooperative interactions might indeed be expected to reduce the relaxation times.

Our susceptibilities above 4°K. agree, within experimental error, with the equation given by McKim and Wolf⁹ for their experimental data on potassium ferricyanide. Below 3°K. our results are from 3 to 7% higher than theirs. The difference is reflected mainly in a less rapid drop in $\chi_m T$ for our measurements. (McKim and Wolf use an equation of different form from ours, but with a correction term corresponding approximately to a Weiss Δ of 0.200, compared with our 0.140.) The differences between our results and theirs are of the same order of magnitude as the differences they observed between the susceptibility of the powdered specimen and values calculated for the powder from the principal susceptibilities of crystalline specimens.

McKim and Wolf⁹ estimated the magnetic heat capacity in zero field as $0.08/T^2$ ($\pm 20\%$) on the basis of a measurement of the adiabatic susceptibility at 1,000 gauss, 1.05°K. The heat capacity at 1.05°K. is in fact slightly over 0.11 (their estimate 0.07). However, this temperature is below the maximum in the heat capacity, and the actual magnetic heat capacity in the $1/T^2$ region is more than twice their estimate.

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[CONTRIBUTION FROM THE ROHM & HAAS COMPANY, REDSTONE ARSENAL RESEARCH DIVISION, HUNTSVILLE, ALABAMA]

The Preparation and Reactions of Dialkylamino Derivatives of Aluminum

By JOHN K. RUFF

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Two different types of dialkylamino derivatives of aluminum, $(R_2N)_2AlX$ and $(R_2N)_3Al$, were prepared. Apparent molecular weights of the products were determined and their structures discussed. Exchange reactions with boron trichloride were interpreted in terms of reactivity of the different types of dialkylamino groups.

Dialkylamino derivatives of aluminum have been discussed only briefly in the literature. Davidson and Brown¹ first reported the preparation of dimethylamino dimethyl aluminum from dimethylamine and trimethyl aluminum. In 1955 tris-dimethylamino alane, bis-dimethylamino alane and dimethylamino alane² were reported by

(1) N. Davidson and H. C. Brown, *J. Am. Chem. Soc.*, **64**, 316 (1942).

Wiberg.³ Recently several other aluminum derivatives containing one dimethylamino group were prepared.⁴ This paper presents further results on the preparation and reactions of aluminum derivatives containing two or more dialkylamino groups.

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