Spin Paramagnetism of Cr^{+++}, Fe^{+++}, and Gd^{+++} at Liquid Helium Temperatures and in Strong Magnetic Fields

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A quantitative experimental study of space quantization of magnetic dipoles and quenching of orbital angular momentum has been made by measuring the fractional variation of the magnetic moment of paramagnetic ions with magnetic field strength at fixed temperatures. The study of trivalent chromium ion ($^4F_{3/2}$ state for free ion) in potassium chromium alum up to 99.5 percent saturation at 1.29°K and in a field of 50,000 gauss gave a close confirmation of space quantization of magnetic dipoles through compatibility of experimental results with the Brillouin function and very marked incompatibility with the Langevin function. The quenching of orbital angular momentum by the crystalline electric field was demonstrated by the agreement of experimental measurements with a Brillouin function for $g=2$ ($L=0$) as against $g=2/5$ ($L=3$). The paramagnetic saturation of iron ($^6S_{5/2}$ for free ion) ammonium alum and gadolinium ($^8S_{7/2}$ for free ion) sulfate octahydrate was achieved, thus permitting of speculation as to a small contribution of the crystalline field to the magnetic moment. Some preliminary calculations were made of this effect for iron ammonium alum and compared with experiment. Experimental study of moments consisted in moving a spherical sample with respect to a double coil system and measuring the flux change ballistically. Magnetic moments were reproducible to ~0.2 percent in mid-range and the magnitude of H/T is known to ~1.5 percent.

ANALYSIS of measurements[1] of magnetic moments of the trivalent chromium ion in potassium chromium alum in the range near paramagnetic saturation has made possible a critical examination of existing simple theories of paramagnetism. In particular, evaluation of ideas regarding the space quantization[2] of magnetic dipoles and the quenching[3] of orbital angular momentum has been made. The idea of space quantization is examined by comparison of the variation of experimental magnetic moments with theoretical predictions, using H/T as independent variable. Two simple formulas, taking into account saturation effects, are the Langevin[4] formula, based on a classical dipole which can assume all orientations in space and the Brillouin[2] function, limited to discrete values of spatial orientation.

The method of checking the idea of quenching of orbital angular momentum is to compare the array of experimental moments with an array of calculated moments for a substance for which $L\neq 0$ for the free ion and in which a nonlinear aggregate[3] of atoms (i.e., not lying on a straight line) contribute to the crystalline field. The trivalent chromium ion in potassium chromium alum meets these requirements, since it exists in a $^4F_{3/2}$ state for the free ion and in the alum the ion is at the center of an octahedron in which water molecules are at the corners. Thus, in one experiment, answers to the questions on space quantization and the quenching of orbital angular momentum are simultaneously obtained.

The investigation of the magnetic field dependence of magnetic moments was extended to trivalent iron ($^6S_{5/2}$ state for free ion) in iron ammonium alum and to trivalent gadolinium ($^8S_{7/2}$ state for free ion) in gadolinium sulfate octahydrate. Since $L=0$ for these ions, interpretation of small, second-order departures of moments from simple functions is made easier, in that the question of incomplete quenching does not arise.

EXPERIMENTAL WORK

The relative magnetic moments were measured with a magnetic moment differential fluxmeter as a function of static magnetic fields for fixed values of temperatures in the liquid helium range. A schematic diagram of the general experimental arrangement is shown in Fig. 1.

The Temperature

The sample (a solid sphere) of potassium chromium alum 2 cm in diameter was kept in contact with liquid helium in a metal Dewar (the vacuum chamber around the sample having been removed), Fig. 1, similar to one previously[5] described. A cylindrical space 6 cm in diameter was available. The value of the initial temperature, 4.21°K, was determined by the local atmospheric pressure and the distance from the sample to the helium level. This temperature varied only slightly with the normal variations of atmospheric pressure or the change in level of the liquid helium. Other temperatures were produced by reduction of pressure above the liquid helium and were kept constant by means of a manostat,

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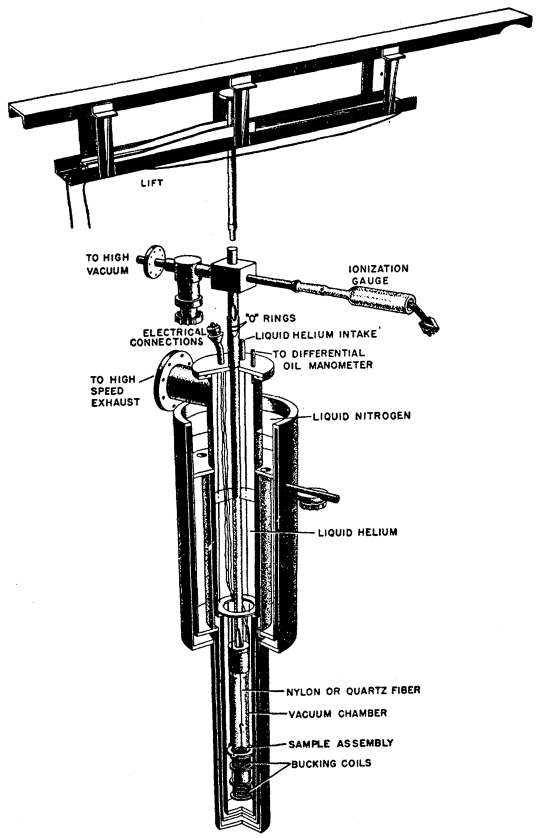

FIG. 1. Schematic diagram of assembly of metal Dewar for liquid helium and sample; displacement lift is shown at top.

except at the lowest temperature. The temperatures were obtained from vapor pressures and monitored by a carbon resistance thermometer.[6] Mercury manometers were used to read vapor pressures in the high pressure range, while oil manometers were used for the low pressure range. In general, the temperatures were decreased monotonically with time to insure temperature equilibrium in the helium I range. However, if temperature inversion occurred with accompanying temperature gradients, variation of the magnetic field could be used to restore equilibrium through eddy current heating of the Dewar metal. The temperatures could be determined to within 0.2 percent for 4.21°K and to 0.5 percent for 1.30° and 2.00°K.

Magnetic Fields

A Bitter[7] type solenoidal magnet, capable of producing fields of over 50,000 gauss, was used. There was available a 10-cm opening with the center and most homogeneous portion of the field 32.5 cm from the top. The magnet was calibrated in gauss produced at a point per ampere of current passing through the magnet; a standardized coil was connected in series with a ballistic galvanometer which was standardized for each set of conditions. Flux change through the coil was generated by moving the coil from the field to be measured to nearly zero field in a time short compared with the period of the galvanometer. Thus, after calibration, the magnetic field was determined by potentiometric measurement of the current through a calibrated shunt resistance in series with the magnet. Fields could be reproduced to within 0.2 percent in the middle of the range, as indicated by reproducibility of magnetic moments. The magnitude of field was known to better than 1 percent.

The Magnetic Moment Differential Fluxmeter[8]

This device consisted of a sample displacement lift (Fig. 1), and a flux change indicator comprised of a self-bucking coil system in series with a controllable resistance and a ballistic galvanometer with a 27-second period. The sample displacer was designed to avoid mechanical shock and motion of the coil system with respect to the magnet. The coil system consisted of about 2000 turns of No. 40 wire on each of the oppositely would bobbins (3.5 cm in diameter). The measurements were made by causing the sample to shuttle, in about 0.5 second, from the middle of one coil to the middle of the other. The positions at the ends of the 4-cm excursions were reproduced to ± 0.003 cm. The net flux change in the coils (due to the motion of the sample), and accordingly the deflection of the ballistic galvanometer, was proportional to the moment of the sample.

INTERPRETATION OF RESULTS

A plot of the experimental results, in which the relative magnetic moment M_r is plotted against H/T, is given in Fig. 2. The interpretation of these results embraces their analysis in the light of space quantization of the ionic moments and the quenching of orbital angular momentum with the idea of detecting departures from known theoretical functions. Since the Langevin and Brillouin functions are unique and proper functions of (H/T), it is sufficient to use relative mag-

TABLE I. Comparison of theoretical and experimental moments for two sets of values of H and T corresponding roughly to the same value of H/T.

	Calculated moments		
	Brillouin $g=2$ $S=5/2$	Space quantized model with cubic field splitting	Experimental moments
$H=35{,}770$ g $T=4.21$°K	4.074	4.067	4.0_6
$H=12{,}200$ g $T=1.32$°K	4.20	4.17	4.1_4

[6] J. R. Clement and E. H. Quinnell, Proc. International Conf. on Low Temperature Physics, Oxford, 1951, p. 51; Rev. Sci. Instr. **23**, 213 (1952).

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netic moments for our analysis. This analysis consists of normalizing the calculated and experimental values at chosen values of H/T. Although space quantization and the quenching of orbital angular momentum are unmistakably indicated by the good agreement of simple theory and experiment for the $^4F_{3/2}$ state of the free chromium ion, there appears to be a small, second-order departure of the experimental results from the Brillouin function. In searching for the source of the small systematic deviation, one must consider the following: (1) experimental error in the measurement of M, H, and T, (2) dipole-dipole interaction, (3) exchange interaction, (4) incomplete quenching, and (5) the effect of the crystalline field splitting on the magnetic energy levels. The diamagnetic contribution is, of course, too small to affect the results.

It is felt that since the moment can be reproduced to 0.2 percent and the magnitude of H/T is known to less than 1 percent, especially for 4.21°K, experimental error as a complete explanation must be discarded. It is true that the field seen by the ion is the applied field with corrections due to the demagnetization factor[9] and the Lorentz polarization[10] (effect of field of neighboring ions). However, since the sample is spherical, these two opposing corrections cancel[11] each other in first approximation. Therefore, any error thus introduced is a second-order correction to a second-order effect which is negligible. For potassium chromium alum, the chromium ions are greatly separated, practically eliminating dipole-dipole and exchange interactions (ignoring the possibility of superexchange based on the existence of excited states of normally diamagnetic atoms).

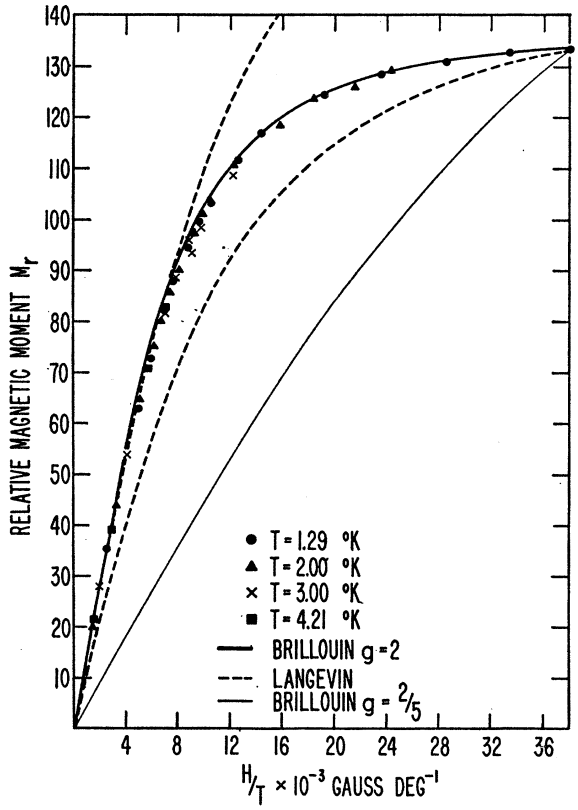

FIG. 2. Plot of relative magnetic moment, M_r, *vs* H/T for potassium chromium alum. The heavy solid line is for a Brillouin curve for $g=2$ (complete quenching of orbital angular momentum) and $J=S=3/2$, fitted to the experimental data at the highest value of H/T. The thin solid line is a Brillouin curve for $g=2/5$, $J=3/2$ and $L=3$ (no quenching). The broken lines are for a Langevin curve fitted at the highest value of H/T to obtain the lower curve and fitted at a low value (slope fitting) of H/T to obtain the upper curve.

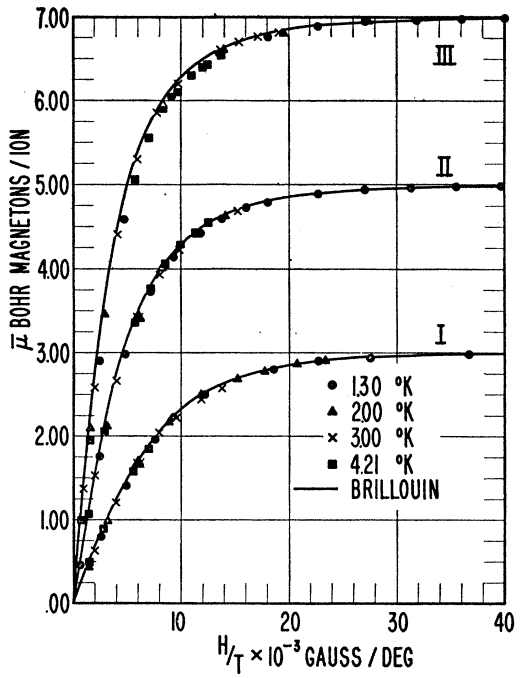

FIG. 3. Plot of average magnetic moment per ion, $\bar{\mu}$ *vs* H/T for (I) potassium chromium alum ($J=S=3/2$), (II) iron ammonium alum ($J=S=5/2$), and (III) gadolinium sulfate octahydrate ($J=S=7/2$). $g=2$ in all cases, the normalizing point is at the highest value of H/T.

Experiments which were carried out with iron ammonium alum[12] (iron in $^6S_{5/2}$ state for the free ion) and gadolinium ($^8S_{7/2}$ state for free ion) sulfate octahydrate show (Fig. 3) slight departures from the Brillouin functions for free spins. Since L is zero for both free ions, these slight departures which remain for the two ions are not attributable to incomplete quenching. Energy levels taken from Kittel and Luttinger[13] and based on the effect of a crystalline cubic field through spin-orbit interaction,[14] have been used to calculate magnetic moments at a few points for iron ammonium alum in

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[12] Contamination and decomposition were carefully avoided.
[13] C. Kittel and J. M. Luttinger, Phys. Rev. **73**, 162 (1948).
[14] J. H. Van Vleck and W. G. Penney, Phil. Mag. **17**, 961 (1934).

mid-range as a function of H, T and the total electric field splitting in zero magnetic field. The calculations consisted in forming a partition function

$$Z=\sum_{i=1}^{6} e^{-E_i/kT},$$

in which the E_i are the energy levels[13] for cubic symmetry which depend on the magnetic field and on crystalline field splitting in zero magnetic field. The magnetic moment is

$$M=kT\partial \ln Z/\partial H.$$

The results of a sample calculation of two points for Fe^{+++} are given in Table I for the (100) direction.

The experimental determination of relative magnetic moments for potassium chromium alum in fields up to 50,000 gauss has shown with precision the creditability of space quantization of magnetic dipoles and the quenching of orbital angular momentum by compatibility of the Brillouin function, for $g=2$, with experiment. Even the small, second-order departure of the magnetic moment from the Brillouin function can probably be attributed, at least in part, to an effect of the crystalline field splitting on the magnetic energy levels, as is suggested by a preliminary calculation of the moment for Fe^{+++} at a few points. More detailed calculations of the effect of the crystalline field are being made and will be reported later.

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Total Cross Sections for 14-Mev Neutrons*

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The total cross sections of over 50 elements were measured in good geometry for 14-Mev neutrons. A plot of the square root of the total cross section *versus* the one-third power of the atomic weight shows deviations from the linear relationship predicted by statistical theory. The deviations are most pronounced for the heaviest elements.

INTRODUCTION

ONE of the methods for determining nuclear radii is based on measurements of the total cross sections of nuclei for fast neutrons. Nuclear radii are most likely to be calculable from such measurements if the neutron wavelength divided by 2π is small compared to the nuclear radius, but not small enough that the nucleus is transparent for the neutrons used. Neutrons of energies of the order of 20 Mev satisfy these conditions. Several measurements using neutrons of energies between 13 and 25 Mev have been published,[1–6] and have served to determine nuclear radii. Each investigation covers a relatively small number of elements. Measurements performed at different neutron energies and in different geometries are difficult to compare particularly because of the strong angular dependence of diffraction scattering about which only very limited experimental information is available.

All the published measurements at neutron energies of the order of 20 Mev are compatible with the assumption that for nuclei heavier than Be the nuclear radius is a linear function of the one-third power of the number of nucleons in the nucleus. The present investigation was undertaken to study possible deviations from this relationship as might perhaps occur in nuclei with closed shells. For this purpose the cross sections of all readily available elements were measured for neutrons of the same energy and in about the same geometry. The uniformity of the technique used for all the elements serves to increase the precision of the cross section *versus* atomic weight relationship and hence might facilitate the interpretation of the data.

PROCEDURE

Fast neutrons were produced by bombarding a thick Zr-T target with 220-kev diatomic deuterium ions. The direction of observation was at an angle of 88° with respect to the deuteron beam. In this direction the neutrons have an energy of 14.12 ± 0.04 Mev, assuming a reaction energy of 17.58 ± 0.02 Mev for the d-T reaction.

A *trans*-stilbene scintillator served as neutron detector. It was placed at a distance of 165 cm from the neutron source. In order to check the sensitivity of the detector to γ-rays or neutrons which do not come directly from the target, a copper bar, 1 in. in diameter and 25 in. long, was inserted between source and detector. It was found that the background counting

* Work performed under the auspices of the AEC.
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