# Hyperfine Field and Ground-State Spin Alignment in Antiferromagnetic $KMnF_3$

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The specific heat of antiferromagnetic $KMnF_3$ at low temperatures has been measured and the contribution of the $Mn^{55}$ polarization extracted. The hyperfine field, when expressed as a frequency, is found to be $A^{55}\langle S\rangle/h=686\pm10$ Mc/sec. $A^{55}$ has been separately measured for $KMgF_3:Mn^{2+}$, and the result is corrected to give $A^{55}$ for $KMnF_3$ at low temperature. By comparison of the two experiments, the ground-state spin alignment of the antiferromagnet is found to be $\langle S\rangle/S=(99.8\pm1.5)\%$, in disagreement with spin-wave predictions.

## INTRODUCTION

BECAUSE the exact ground-state spin alignment of a three-dimensional antiferromagnet is not known theoretically, an experimental determination is of interest. $KMnF_3$ is an attractive antiferromagnet from a theoretical point of view because its nearly cubic structure gives rise to low anisotropy energy and to predominance of nearest-neighbor interactions. Experimentally $KMnF_3$ is attractive not only for the above reasons but also because a considerable amount is known about its properties. In these experiments we determine the hyperfine field, $A^{55}\langle S\rangle$, directly from the specific heat and then compare the result with the precise determination of $A^{55}$ obtained by correction of electron paramagnetic resonance (EPR) results in an isomorphous dilute salt. We shall describe the experiments briefly and then discuss the results.

## SPECIFIC HEAT

The measurements were made in a cryostat which has been used by one of us (H. M.) for several years for accurate determination of electronic specific heats. The essential feature of the cryostat is a mechanical heat switch. The $KMnF_3$ powder specimen, which was compacted in a thin-walled copper calorimeter, could be cooled from room temperature to 1.1°K in a high vacuum so that the spurious heat of adsorption of exchange gas was avoided. The carbon resistance thermometer was contacted to the specimen by a heavy copper wire wound around the resistor, extended into the pill-like specimen and cemented with GE7031. Isolation of the specimen within the cryostat was sufficiently good that a thermal response time of three minutes presented no difficulty. During calibration of the resistor, immediately following the specific heat run, exchange gas was introduced to insure equilibrium between the resistor and the helium bath. Below 1.5°K, the resistor was calibrated against a $He^3$ vapor pressure thermometer. Two complete runs were made. The heat capacity of the addenda, including calorimeter, heater, etc., was determined from a third run. The specific heat data were analyzed by a least-squares fit to the function

$$cT^2=a+bT^5,$$

where $c$ is the molar specific heat. The term $bT^5$ presumably contains the spin-wave specific heat as well as the lattice. Orbach[1] has shown that the spin-wave spectrum for a canted antiferromagnet is very little altered from that of a normal antiferromagnet (for $KMnF_3$, $M/M_s=1.4\times10^{-3}$); furthermore, the spin-wave energy gap should be well below 1°K in this material owing to the low anisotropy. Thus the $T^3$ spin-wave specific heat is likely to hold well in $KMnF_3$, and indeed, a slight departure from linearity which was found in the $cT^2$ vs $T^5$ plot was so small as to be indistinguishable from systematic error. The results of the least-squares fit are $a=26.3\pm0.7$ mJ°K/mole and $b=0.387\pm0.006$ mJ/mole °K$^4$. The errors quoted are rms deviations of 32 points between 1.230 and 2.742°K.

## ELECTRON PARAMAGNETIC RESONANCE

The electron paramagnetic resonance (EPR) of $Mn^{2+}$ was observed in a single crystal of $KMgF_3$. The $Mn^{2+}$ was present as an impurity in the "pure" crystal. The high-sensitivity $X$-band spectrometer used was of a conventional design. The temperature dependence of the hyperfine interaction has been extensively investigated, and an empirical $T^{1.5}$ dependence has been found.[2] Using this dependence, the value of $A^{55}$ for $KMgF_3:Mn^{2+}$ was extrapolated to $[91.26(4)\pm0.05]\times10^{-4}$ at 0°K.[3]

The value of $A^{55}$ for $KMnF_3$ at low temperature is calculated using the results of four separate experiments. First, the precise volume of the somewhat distorted

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[1] R. Orbach, Phys. Rev. **115**, 1189 (1959).
[2] W. M. Walsh, Jr. (to be published).
[3] $A^{55}$ for $KMgF_3:Mn^{2+}$ has been measured by S. Ogawa, J. Phys. Soc. Japan **15**, 1475 (1960). He obtains $A^{55}=(91.2\pm0.9)\times10^{-4}$cm$^{-1}$, in agreement with our result. In view of the necessarily large uncertainty in the specific heat, we felt a more accurate determination of $A$ was required.

fluorine octahedron in $KMnF_3$ is obtained from the low-temperature x-ray data.[4] Second, the Mn—F bond distance in $KMgF_3$ has been determined from the analysis of the $F^{19}$ resonance in $KMnF_3$.[5] Finally, the volume dependence of the hyperfine interaction has been determined directly by high-pressure EPR experiments on $MgO:Mn^{2+}$.[6] The value of the volume dependence of $A^{55}$ in octahedral fluorine coordination may be inferred from the EPR experiments of Ogawa[3] on $Mn^{2+}$ in $KMgF_3$, $K_2MgF_4$, $KCdF_3$, and $KCaF_3$ by plotting $A$ vs $(M-F)^3$. We obtain the same value of $\partial \ln A/\partial \ln V=0.06$ from both experiments. Since the magnitude of the volume correction is small, any effect on $A$ due to the slight departure from octahedral symmetry in $KMnF_3$ will be negligible. We finally obtain for $KMnF_3$, $A^{55}=[91.64(7)\pm 0.05]\times 10^{-4}$ cm$^{-1}$.

## DISCUSSION

The nuclear contribution to the specific heat is

$$cT^2/R=\tfrac{1}{3}I(I+1)(A^{55}\langle S\rangle/k)^2.$$

No contribution from $F^{19}$ polarization is included since the F ion is situated midway between its antiferromagnetically aligned Mn neighbors. Thus, we obtain from experiment $A^{55}\langle S\rangle=(229\pm 3)\times 10^{-4}$cm$^{-1}$, or

$$A^{55}\langle S\rangle/h=(686\pm 10)\text{ Mc/sec.}$$

Recently, double resonance experiments were reported[7] in which the $Mn^{55}$ resonance could be excited at frequencies as low as 600 Mc/sec. The discrepancy arises from nuclear-electron coupling and will be described in a future publication.[8] The detailed analysis of the $Mn^{55}$ excitation, however, yields a frequency of $(689\pm 2)$ Mc/sec in the limit of no electron coupling, in good agreement with our result.

Comparing the specific heat and the EPR results, we obtain

$$\langle S\rangle/S=(99.8\pm 1.5)\%.$$

In contrast to the experimental result, spin-wave theory[9] predicts a 3% reduction spin, in which is comfortably outside our experimental error. We note again that the presence of canting in $KMnF_3$ does not appreciably affect the theoretical estimate of $\langle S\rangle$, since the spin-wave spectrum itself is only slightly altered.

Two previous experiments have been reported which give information on the ground-state spin configuration. Clogston *et al.*[10] made a comparison of EPR measurements and specific heat data of Cooke and Edmonds[11] in a manner similar to that above, and found an alignment of $(101\pm 2)\%$ for $MnF_2$. Walsh and Rupp[12] were able to compare their EPR results on trivalent $Fe^{57}$ in ZnO with the nuclear magnetic resonance results of Robert[13] on YIG and concluded that any reduction of sublattice magnetizations in YIG must be less than 2% and very likely less than 1%. The spin-wave calculation of the effect of zero-point energy is itself only approximate, and an alternate perturbation calculation has been proposed by Walker[14] which gives a smaller reduction of $\langle S\rangle$, in agreement with experimental evidence.

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