

Phase diagram of antiferromagnetic $K_2[FeCl_5(H_2O)]$ Fernando Palacio,* Armando Paduan-Filho,[†] and Richard L. Carlin*Department of Chemistry, University of Illinois at Chicago Circle,**Chicago, Illinois 60680*

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The boundaries between the paramagnetic, antiferromagnetic, and spin-flop phases of $K_2[FeCl_5(H_2O)]$ have been determined by means of ac susceptibility measurements in an applied magnetic field. With $T_c(0) = 14.06$ K, we find the bicritical point at 13.6 K and 34.1 kOe, $H_{SF}(0) = 26$ kOe, and derive $H_A = 1.7$ kOe, and $H_E = 199$ kOe. Similarly, for $Rb_2[FeCl_5(H_2O)]$, $T_c(0) = 10.03$ K, $T_b = 10$ K at 18 kOe, $H_{SF}(0) = 14$ kOe, $H_A = 0.6$ kOe, and $H_E = 172$ kOe. The anisotropy fields appear to be anomalously low.

The series of antiferromagnetic compounds $A_2[FeX_5(H_2O)]$ has recently been of interest.¹⁻⁴ The cation A^+ may be Cs^+ , Rb^+ , NH_4^+ , or K^+ when X^- is chloride, and Cs^+ or Rb^+ when the halide is Br^- . All the materials are orthorhombic and consist of discrete octahedra linked together only by hydrogen bonding.⁴⁻⁶ The ordering temperatures in zero-external-field range from 6.57 K for $Cs_2[FeCl_5(H_2O)]$ to 22.90 K for $Rb_2[FeBr_5(H_2O)]$; two of the compounds each exhibit two peaks in the specific heat separated by about 1 K, which is suggestive of spin reorientations. The Cs,Cl salt provides a good example of the nearly-simple-cubic Heisenberg $S = \frac{5}{2}$ antiferromagnet,² but there is some evidence for significant lower-dimensional magnetic ordering in several of the other salts.^{1,3} We have found, for example, that the zero-field susceptibilities of $Rb_2[FeCl_5(H_2O)]$ cannot be fit by the same model that was applied to $Cs_2[FeCl_5(H_2O)]$.² Rather, these susceptibilities have been fit by a linear-chain model, but with an important molecular-field (or three-dimensional) correction.^{1,4}

A useful procedure for determining the parameters which describe a magnetic system is to determine the phase boundaries in the H - T plane. In weakly anisotropic systems such as are under discussion here, a spin-flop (SF) phase is anticipated in addition to the paramagnetic (P) and antiferromagnetic (AF) phases. The three boundaries separating these phases meet at the bicritical point. The phase diagram of $Cs_2[FeCl_5(H_2O)]$ was determined and reported earlier, and we present here a detailed report on the potassium analog, $K_2[FeCl_5(H_2O)]$. Attempts to measure the phase boundaries of several of the other salts in this series will also be described. Although a number of phase diagrams of hydrated halides of isoelectronic manganese(II) have been reported, this series of measurements appears to be the first on the phase diagrams of iron(III) salts.

The compound $K_2[FeCl_5(H_2O)]$ belongs to the

space-group $Pnma$ and contains four crystallographically equivalent molecules in a unit cell. The other crystallographic features and a discussion of the likely superexchange paths have been presented elsewhere.³ The ordering temperature in zero-external field, $T_c(0)$, is 14.06 ± 0.01 K.

I. EXPERIMENTAL

The phase boundaries were obtained by measuring the differential magnetic susceptibility in an external magnetic field provided by a superconducting solenoid capable of producing 65 kOe. The magnetic susceptibility could be measured between 1.6 and 30 K by an ac mutual inductance method. The installation has been described in detail elsewhere.⁷ The samples, which were prepared by the evaporation of aqueous solutions, were oriented with the easy axis parallel to the external field.

II. RESULTS

The susceptibility at constant temperature of $K_2[FeCl_5(H_2O)]$ behaved as anticipated as the applied field was varied: sharp peaks were observed as the AF-SF boundary was crossed, while changes in the slope were found as the other boundaries were crossed. The resulting phase diagram is illustrated in Fig. 1. The bicritical point occurs at $T_b = 13.6 \pm 0.1$ K and $H_b = 34.1 \pm 0.1$ kOe, and the $H_{SF}(0)$, the spin-flop field extrapolated to 0 K, is 26 kOe. The error limits quoted refer to uncertainties in the measurement of both temperature and magnetic field. Using the reported³ $\chi_1(0) = 0.07$ emu/mole, these results allow one to calculate the anisotropy field, H_A , as 1.7 kOe, and the exchange field, H_E , as 199 kOe. External fields of more than 400 kOe would be required in order to measure these quantities directly. The ratio $\alpha = H_A/H_E = 8.5 \times 10^{-3}$.

The relationships used above are the usual molecu-

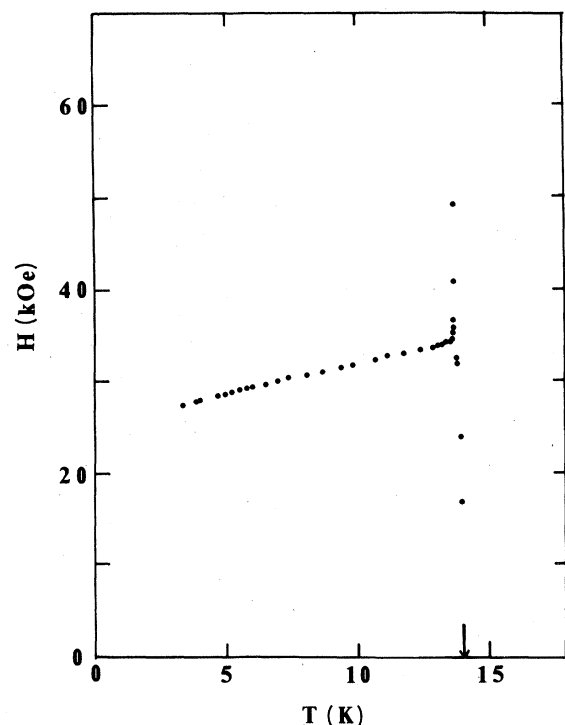


FIG. 1. Magnetic phase boundaries of $K_2[FeCl_5(H_2O)]$.

lar field results, that $H_{SF}(0) = (2H_E H_A - H_A^2)^{1/2}$ and $\chi_1(0) = 2M_s / (2H_E + H_A)$, where $M_s = \frac{1}{2} N g \mu_B S$ is the saturation magnetization of one magnetic sublattice.⁸

III. DISCUSSION

We observe that these results show that $K_2[FeCl_5(H_2O)]$ is a good example of the $S = \frac{5}{2}$, three-dimensional Heisenberg antiferromagnet. In particular, the quantity α defined above has been taken as a guide to the ideality to which a system behaves as a magnetic model system. The value of α determined here is even smaller than that reported earlier for both $Cs_2[FeCl_5(H_2O)]$ and MnF_2 ,⁹ both good examples of this magnetic model system. Since both $T_c(0)$ and T_b lie in conveniently accessible temperature regions, one anticipates that this material will be of interest for future critical-point studies.

The evaluation of H_E allows the exchange constant to be calculated directly from the relationship $g \mu_B H_E = 2z|J|S$, and we find $zJ/k = -5.4$ K. This may be compared with the value -6.2 K calculated from $2J/k_B + zJ'/k_B$, where the latter values were obtained from an analysis of the zero-field susceptibilities in terms of a magnetic linear chain with a large molecular-field correction.³ Since the specific heat of this system provides little evidence for linear chain behavior, the value reported here is probably more accurate.

There are several other interesting facets to these results. First of all, we find the AF- P phase boundary to be almost vertical; the ratio $T_b/T_c(0) = 0.97$. A number of other weakly-anisotropic antiferromagnets such as $Cs_2[FeCl_5(H_2O)]$,² $CuCl_2 \cdot 2H_2O$,¹⁰ and¹¹ MnF_2 behave similarly. Second, the derived anisotropy fields appear to be anomalously small. Several of the more important factors that are usually assigned as sources of the anisotropy field are single-ion anisotropy, dipole-dipole interaction, and anisotropic exchange.⁹ The anisotropy field in similar compounds of isoelectronic manganese(II) is generally ascribed¹² to zero-field splitting. From the relationship $g \mu_B H_A = 2|D|(S - \frac{1}{2})$, we derive the result $|D/g \mu_B| = 425$ Oe, yet the zero-field splitting of iron(III) doped into the isostructural salt $(NH_4)_2[InCl_5(H_2O)]$ was determined¹³ by EPR at 77 K as $|D/g \mu_B| = 1.9$ kOe, and furthermore a rhombic (E) term about 16% as large was also observed. If we assume that these parameters may also be applied (if only to order of magnitude) to the compounds investigated here, the overall splitting of the 6S manifold by the D term alone would be of the order of 10 kOe. Anisotropic exchange is not important in these materials. Dipole-dipole interactions should be small, but perhaps they act in opposition to the other contributors to the anisotropy field. We can offer no other explanation for the occurrence of such small anisotropy fields, but the result is interesting because it allows this salt to follow the Heisenberg magnetic model more closely.

Experiments were also carried out on several other salts, all of which are isostructural among themselves and with the previously mentioned crystals. The spin-flop boundary was easily observed and delineated in $Rb_2[FeCl_5(H_2O)]$. We find $T_b = 10.0 \pm 0.1$ K at $H_b = 18.0 \pm 0.2$ kOe, and $H_{SF}(0) = 14$ kOe. This allows the determination that $H_A = 0.6$ kOe, $H_E = 172$ kOe, and $\alpha = 3.4 \times 10^{-3}$. Unfortunately, we had great difficulty observing the AF- P and SF- P boundaries and did not pursue the point when we learned of the results of O'Connor and co-workers⁴ on the same material. Our data show, nevertheless, that this salt is also a good example of the Heisenberg model system. The anisotropy field is quite small once again.

Despite great care, we were also unable to observe any of the phase boundaries of either $Cs_2[FeBr_5(H_2O)]$ or $Rb_2[FeBr_5(H_2O)]$. Thus, no spin-flop boundary of $Rb_2[FeBr_5(H_2O)]$ was found below 55 kOe; this material has a high transition temperature (22.9 K) and its susceptibility near $T_c(0)$ does not change very much. Apparently our method of measurement is not suitable for this salt.

The last sample we examined was $(NH_4)_2[FeCl_5(H_2O)]$. This material exhibits³ two small λ anomalies in the specific heat (at 6.87 and 7.25 K) and, in contrast to all of the other salts described here, exhibits in the specific heat evidence

for substantial short-range order. The susceptibility below 30 K varies only slightly with temperature, and, although antiferromagnetic ordering was clearly observed, no easy axis was observed. This result was ascribed to a canting of the spins. Nevertheless, we examined crystals with fields parallel to the a axis (the easy axis in the other systems), but observed no spin-flop transitions.

The question was raised³ why canting was observed in $(\text{NH}_4)_2[\text{FeCl}_5(\text{H}_2\text{O})]$ but not in the potassium salt. Indeed, no canting is observed in any of the cesium or rubidium compounds either. Rather than postulating canting in the ammonium salt, alone of all these isostructural salts, it seems to us that a simpler explanation for this result is that the ammonium salt is the one material in this series which is likely to undergo a crystal phase transition as it cools. In fact, we have preliminary results which suggest that such is the case. It is well known that the ammonium ion is a hindered rotator in the solid state, and it is likely that a reorientational ordering of the ammonium ion causes a relatively high-temperature phase transition.¹⁴ Depending on the nature of this transition, which we are now investigating more carefully, the easy axis will either have a different orientation from that of all of its congeners, or else will exist inhomogeneously on a microscopic scale. Furthermore, it is

likely that the lower-dimensional magnetic behavior found to be so much more important in this material over all of the other analogs is due to atom motion that also arises from the crystal phase transition.

In conclusion, the salt $\text{K}_2[\text{FeCl}_5(\text{H}_2\text{O})]$, along with its congener $\text{Cs}_2[\text{FeCl}_5(\text{H}_2\text{O})]$, is a good example of the nearly simple cubic, $S = \frac{5}{2}$ Heisenberg model antiferromagnet. The rubidium salt appears to exhibit more important lower-dimensional behavior, and a careful study of its magnetic specific heat is in progress in order to clarify this situation. The anisotropy field, interestingly, appears to be anomalously low in all of these crystals.

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