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Magnetic properties of some cubic rare-earth elpasolite hexafluorides

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Single crystals of cubic A_2BRF_6 (A, B = alkali metals, R = rare earth) have been studied magnetically. If R is a Kramers ion, the system orders well below 1 °K. For non-Kramers ions, we find in general Van Vleck behavior at low temperature. Crystal-field splittings are found to be in poor agreement with point-charge model calculations. Besides crystal-field aspects, a number of hyperfine properties will also be discussed.

I. INTRODUCTION

In recent years a number of interesting physical phenomena related to crystal-field levels have been observed, mostly in intermetallic compounds. We think here of their influence on superconductivity,[1-3] transport properties,[3,4] elastic properties,[5,6] nuclear adiabatic cooling,[7] and nuclear ordering phenomena,[8] as well as of the problem of the instability of singlet ground states against overcritical exchange interactions.[9] Also, the question of the origin of crystal fields in intermetallic compounds has received a lot of attention among solid-state scientists.[10-19] In a number of cases, the simple effective-point-charge model (EPCM) was in surprisingly good agreement with experimental results, e.g., in all the PrX compounds having rocksalt-type structure.[10] In metallic systems, the presence of conduction electrons usually presents a great many complications. On the other hand, most of the insulating compounds have lower than cubic point symmetry, making crystal-field analysis difficult. Fortunately, it was discovered recently[20-23] that the rare earths form a number of insulating compounds of the type A_2BRF_6, in which the rare earth has the same point symmetry as in the already explored rocksalt structures. The isomorphous system A_2BRCl_6 has also been explored,[24-26] however, we decided to work with the A_2BRF_6 system, because the latter has a superior stability in air against hydrolysis. A picture of the unit cell is presented in Fig. 1. A few insulating rare-earth compounds with cubic point symmetry have been known for a while, such as, e.g., rare-earth spinels[27] (with some heavy rare earths only) or the divalent RF_2 compounds with fluorite-type structure. The A_2BRF_6 system, however, exists for all R (La-Lu) and thus provides the possibility of systematic studies. We found that Tb and Ho compounds of this type exist in nonmagnetic crystal-field ground states and do not order magnetically which is unusual for Tb and Ho compounds. In these materials it should be possible to observe the Tb and Ho nuclear magnetic resonance in relatively low fields (a few hundred Oe) at conventional NMR frequencies. The relatively large hyperfine enhancement of the local field at the rare-earth nuclei make Tb and Ho compounds potentially interesting for nuclear magnetic studies and possibly for the observation of a nuclear magnetic phase transition at low temperature.[8] Finally, we would like to point out that the Knight shift of Eu^{3+} was calculated over a decade ago by Elliott[28] but has never been observed to the best of our knowledge. Cubic Eu^{3+} systems such as Rb_2NaEuF_6, Cs_2NaEuF_6, and Cs_2KEuF_6 would be ideally suited for such a study, because the $J=1$ state is not crystal-field split and the Van Vleck susceptibility can be used to derive the spin-orbit coupling constant. The results may be compared with other cubic metallic Eu^{3+} compounds such as $EuPd_3$, $EuBe_{13}$, $EuRh_2$, etc. and the conduction-electron contribution evaluated.

II. EXPERIMENTAL PROCEDURE

A. Preparation of single crystals

The alkali fluorides used in the preparation of the $A_2^{I}B^{I}R^{III}F_6$ compounds were high-purity single crystals which were prepared by zone-refining reagent-grade compounds. The rare-earth fluorides were made from high-purity rare-earth oxides (min 99.99%) by hydrofluorination and subsequent zone refining. Those rare-earth fluorides which do not undergo a severe crystallographic phase change between the melting point and room temperature were made as single crystals. The others were of the same high purity but quite polycrystalline. A typical procedure for the crystal growth of the $A_2^{I}B^{I}R^{III}F_6$ compounds was the following: A stoichiometric mixture of the crystals were admixed and placed in a Pt boat. The boat was put into a zone-melting apparatus and melted down in a dry N_2 atmosphere. A molten zone of approximately 20% of the length of the boat was established and made to traverse the ingot at 3–5 mm per hour. Typically the results were a mixed phase at the beginning of the ingot followed by a clear section of single-phase material and finally a mixed phase at the end. The proportions varied for each compound but were approximately one-third for each section.

Growth of single crystals from incongruently melting multicomponent chemical systems was achieved because the zone-melting technique is unique in that the composition of the liquid differs from that of the solid being formed. By using a slow travel rate, which allows time for diffusion and convection, the narrow molten zone with two liquid-solid interfaces allows the required compositional changes to take place in the liquid zone.

B. Magnetic measurements

Susceptibility vs temperature was measured in a pendulum magnetometer between 1.3 and 300 K in fields up to 15 kOe. Below this temperature, the low-field ac susceptibility was taken by a mutual induction method. The nuclear magnetism of Rb_2NaHoF_6 was measured by a dc flux-gate magnetometer described elsewhere.[29]

III. RESULTS AND DISCUSSION

All our results are summarized in Table I, where the studied compounds are listed in increasing atomic number of the rare earth. We have studied mostly Rb_2NaRF_6 which are known to exist for R from Sm to Lu only.[20] We have also studied Cs_2NaHoF_6 in order to compare it with Rb_2NaHoF_6. The Cs_2Na compounds again form only for R from Sm to Lu,[20] similar to the Rb_2Na combination. In order to include in our study the lighter rare earth we have studied Cs_2KPrF_6 as an example. The Cs_2K combination forms for any rare earth between La and Lu.[20] Geometrical consideration of the phase formation has been thoroughly discussed by Védrine *et al.*[22,23] and we will proceed to discuss magnetic properties.

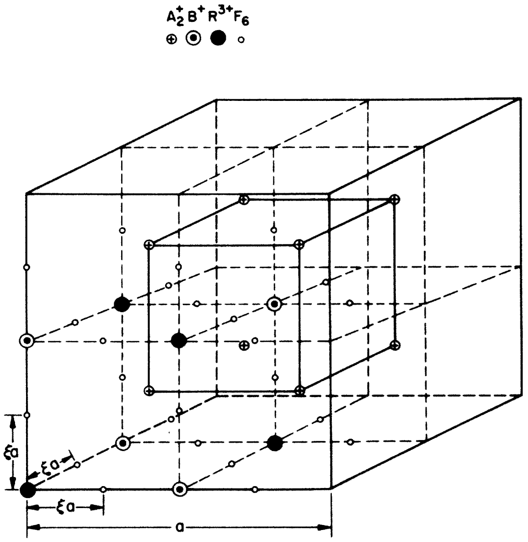

FIG. 1. Picture of the cubic unit-cell of an A_2BRF_6 elpasolite hexafluoride.

A few general remarks are necessary in order to understand the results and calculations. The unit cell shown in Fig. 1 has (besides the lattice constant) one free parameter ξ, the position of the fluorine atoms. Irrespective of ξ, however, the point symmetry on the R site is strictly cubic. The first-neighbor distance d_{R-F} is given by ξa, where ξ has been found to vary between 0.225 and 0.275.[20-23] The second-neighbor distance d_{R-A} is $\frac{1}{4}a\sqrt{3}$ with primitive cubic symmetry, the third-neighbor distance is $d_{R-B}=\frac{1}{2}a$, again in octahedral symmetry. For crystal-field calculations we have considered only the first two neighbors. The first neighbors contribute in general (92–95)% to the crystal field if we assume $Z_F = -|e|$, $Z_A = A_B = +|e|$, and $Z_R = +3|e|$. The crystal-field point-charge potentials can be written using the notation of Lea-Leask-Wolf,[30]

$$B_4 = \tfrac{7}{2}(e^2\langle r^4\rangle \beta/a^5)f_4(\xi)\,, \tag{1}$$

$$B_6 = (e^2\langle r^6\rangle \gamma/a^7)f_6(\xi)\,, \tag{2}$$

where

$$f_4(\xi) = -1/8\,\xi^5 - \tfrac{1}{9}(4/\sqrt{3})^5$$

and

$$f_6(\xi) = -\tfrac{3}{64}(1/\xi^7) + \tfrac{1}{9}(4/\sqrt{3})^7\,.$$

Level splittings were then calculated from the generally diagonalized cubic-crystal-field Hamiltonian given by Lea-Leask-Wolf for all J's.[30] One can see that crystal-field splittings depend sensitively on ξ. Unfortunately, ξ has not been determined specifically for the compounds in which we have performed crystal-field calculations. It was shown, however, that ξ varies between 0.260 and 0.265 in a number of Rb_2NaRF_6 compounds[20] and we chose $\xi=0.265$ for all these compounds. For Cs_2NaHoF_6 we used $\xi=0.275$, a value found for Cs_2NaErF_6.[20] For Cs_2KPrF_6 we took $\xi=0.225$, a number given for Cs_2KYF_6.[22] For $\langle r^4\rangle$ and $\langle r^6\rangle$ we used tabulated data of Freeman and Watson.[31] In some cases comparison is made with relativistic values of Burton-Lewis[32] and the latter give somewhat better agreement with experimental values. From magnetic form-factor measurements it is concluded that relativistic $\langle r^4\rangle$ calculations are in better agreement with experiment.[15,33–35] It is not clear, however, how invariant the $\langle r^4 \rangle$ values are with respect to variable ligands, and this presents a considerable uncertainty in theoretical considerations. For all our calculations we used our own lattice constants. The Rb_2NaRF_6 lattice constants are in good agreement with already established values,[20] and show a perfectly linear relationship if plotted vs atomic R^{3+} radius. We used the same values given by Iandelli[36] in his analysis of rare-earth rocksalt structures. Considerable scatter is observed on Cs compounds. It is possible that one has some partial mutual substitution of A and B sites. Especially our Cs_2KPrF_6 lattice parameter is about 0.1 Å larger than one would expect from the average of previously established values.[20–22] We will now proceed to discuss the individual compounds.

A. Rb_2NaGdF_6

Among the Rb_2Na series this compound was mainly studied to probe the strength of the exchange interaction as we have no complication from crystal fields. Unfortunately, we could not detect any magnetic order above 0.45 K. A $1/\chi$ plot vs T between 0.45 and 300 K yields $\theta_p \approx 0$, suggesting very weak exchange forces. The magnetization curves at 1.30 and 4.21 K give a perfect fit to within 1% to a Brillouin function with $g = 2$ and $J = S = \frac{7}{2}$. We conclude again that exchange effects must indeed be very weak in this system, and in all Rb_2Na phases in general. The dipolar interaction energy between two neighboring Gd spins is only 0.12 K. This makes the analysis of Van Vleck susceptibilities in such compounds very simple in that splittings can be calculated directly without corrections due to exchange interactions.

B. Rb_2NaEuF_6

Our Van Vleck susceptibility of 0.0628 cm^3/mole leads to a spin-orbit coupling constant Δ of 477 K, using the expression[37]

$$\chi(0) = 8 L \mu_B^2 / \Delta , \qquad (3)$$

where Δ is also identical to the E_1-E_0 multiplet splitting. The cubic point symmetry leaves the $J = 1$ state unsplit and no corrections have to be made due to crystal-field splittings. Our spin-orbit coupling constant is in excellent agreement with other values derived from other compounds with cubic point symmetry, such as $EuPd_3$,[38] $EuBe_{13}$,[39] etc. With respect to metallic compounds, no noticeable shift in Δ could be detected. Attempts were made to study the Eu^{151}NMR in this compound at frequencies as low as 2 MHz and fields as high as 15 kOe without success.[40] This, however, is just slightly outside Elliot's[28] predicted Knight-shift value of −89% (i.e., 0.115 kHz/G). Since he neglected core polarization, his number might carry a considerable error bar and the resonance might have possibly fallen into our available field-frequency range. Clearly a search has to be made at lower ν/H ratios.

TABLE I. Summary of magnetic and lattice parameters of a number of rare-earth hexafluorides with elpasolite structure.

Compound	a [a] (Å)	T_N(°K)	χ(0)(cm^3/mole)	H_{hf}/H_0 (=1 + K)	δ
Rb_3PrF_6	not fcc	···	···		
Cs_2KPrF_6	9.696		0.0044	1.82	726° $(E_{\Gamma_4} - E_{\Gamma_1})$
Rb_2NaEuF_6	8.973		0.00628		477 $(E_1 - E_0)$
Rb_2NaGdF_6	8.952	<0.45			
Rb_2NaTbF_6	8.923		0.312	20.5	75.6 $(E_{\Gamma_4} - E_{\Gamma_1})$
Rb_2NaHoF_6	8.881		1.04	138	
Cs_2NaHoF_6	9.073	0.62			
Rb_2NaErF_6	8.859	<0.45			
$Rb_2NaY_{0.9}Er_{0.1}F_6$	8.870	<0.45			
Rb_2NaTmF_6	8.839		0.0569	10.7	251 $(E_{\Gamma_4} - E_{\Gamma_1})$
Rb_2NaYbF_6	8.819	<0.45			

[a] This work.

C. Cs_2KPrF_6

In this compound we expect a level sequence Γ_1-Γ_4-Γ_3-Γ_5 with Γ_1 being the ground state.[30] In Fig. 2 the inverse molar susceptibility is plotted (along with Rb_3PrF_6). The susceptibility levels off below 100 K, and we conclude that Γ_1 is indeed the ground state. The susceptibility $\chi(0) = 0.0044$ cm^3/mole, given by[37]

$$\chi(0) = 2g_J^2 \mu_B^2 \alpha^2 / \delta , \qquad (4)$$

yields a Γ_1-Γ_4 splitting of $\delta = 726$ K ($\alpha^2 = \frac{20}{3}$ for Pr^{3+}). It is interesting to compare this splitting with point-charge calculations. Using $Z_F = -|e|$ for F and $Z_{Cs} = +|e|$ for Cs we find from the Freeman and Watson[31] Hartree-Fock values of $\langle r^4 \rangle$ and $\langle r^6 \rangle$, $\delta = 281$ K, in considerable discrepancy. Relativistic values of Burton and Lewis[32] yield $\delta = 486$ K, still considerably below the experimental value. From the chemical point of view F cannot take a charge stronger than $-|e|$. With only this information we cannot decide whether the effective point-charge model retains some validity or whether our discrepancy is due to excessive values of $A_6 \langle r^6 \rangle$. As noticed previously in other halide crystals,[41] the latter is more likely to be the reason for our discrepancy.

The very low Van Vleck susceptibility leads to a very weak hyperfine enhancement factor H_{hf}/H_0 given by

$$H_{hf}/H_0 = 1 + a\chi(0)/g_J \mu_B g_N \mu_N . \qquad (5)$$

We find for Cs_2KPrF_6, $H_{hf}/H_0 = 1.82$. Here and in all the following calculations of hyperfine enhancement factors we used Bleaney's tabulation[42] of hyperfine constants and the nuclear data table given in the American Institute of Physics Handbook.[43]

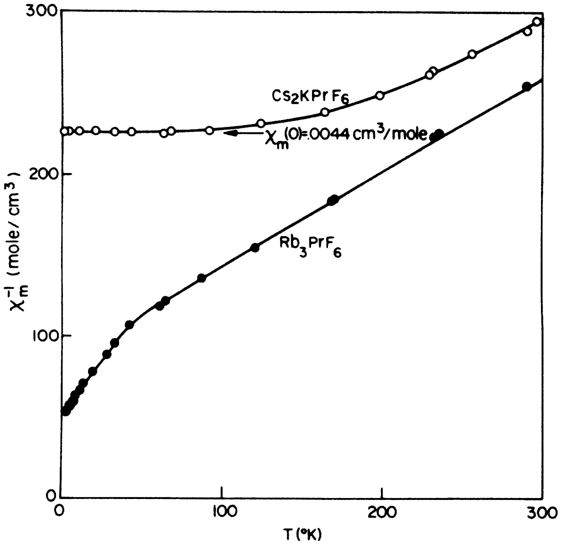

FIG. 2. Inverse molar susceptibility of Cs_2KPrF_6 and Rb_3PrF_6 (noncubic) vs temperature.

D. Rb_3PrF_6

Besse and Capestan[21] reported Rb_3CeF_6 to be cubic. In contrast, we found that Rb_3PrF_6 is not cubic and shows a complex magnetic behavior (Fig. 2). Its structure was not further analyzed; however, it appears to be of very low symmetry.

E. Rb_2NaTbF_6 and Rb_2NaTmF_6

For the heavier rare earths it is more convenient to study the Rb_2NaRF_6 rather than the Cs_2K combination, which is hygroscopic and very unstable in air. In constrast, the Rb_2Na series remains stable and clear in air over years. In Fig. 3 we show the inverse molar susceptibility $1/\chi_m$ vs T of Rb_2NaTbF_6 and Rb_2NaTmF_6. We will discuss them together because they have both the same $J = 6$ ground term and their crystal-field splitting pattern is very similar. Among intermetallic compounds this is generally not true, and all Tb compounds order, whereas Tm compounds often exhibit Van Vleck paramagnetism.

In octahedral symmetry the crystal-field level sequence of both is expected to be[30] Γ_1-Γ_4-$\Gamma_5^{(2)}$-Γ_2-$\Gamma_5^{(1)}$-Γ_3 within an effective point-charge model. The ground state is nonmagnetic as shown in Fig. 3 and we assume it to be Γ_1, although Γ_2 is in

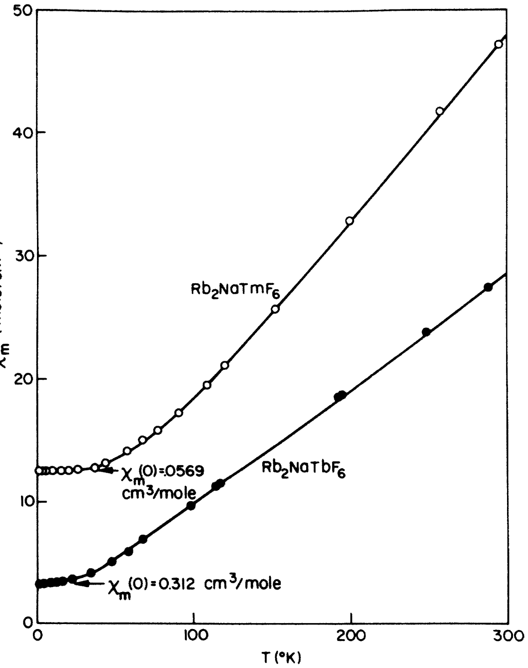

FIG. 3. Inverse molar susceptibility of Rb_2NaTbF_6 and Rb_2NaTmF_6.

principle also possible if sixth-order crystal-field potentials are predominant. From the Van Vleck susceptibility we calculate a Γ_1-Γ_4 splitting of 76 K in the Tb compound and 250 K for the Tm compound. The corresponding point-charge values are 26 and 28 K for nonrelativistic $\langle r^n \rangle$[31] and 39 and 41 K for relativistic $\langle r^n \rangle$.[32] We note here again that the discrepancy between experiment and the point-charge model is considerably worse for the heavy rare earths than for the lighter ones, a fact already noted in the rare-earth monopnictides.[11] It reaches an order-of-magnitude discrepancy. Part of the discrepancy could be removed by assuming a smaller ξ value, leading to larger crystal-field splitting; however, we have no obvious reason why ξ should be smaller in our compounds than in three other compounds of the Rb_2Na type[20] analyzed thus far. We believe that the validity of the EPCM in the monopnictides of the light rare earths is indeed fortuitous,[11] and cannot be generalized.

From our low-temperature Van Vleck susceptibility we can again calculate the hyperfine enhancement factor and we find 20.5 and 10.7 for the Tb and Tm compound, respectively. NMR in a Tb singlet in cubic environment has never been observed and our system would be particularly suitable for such a study.

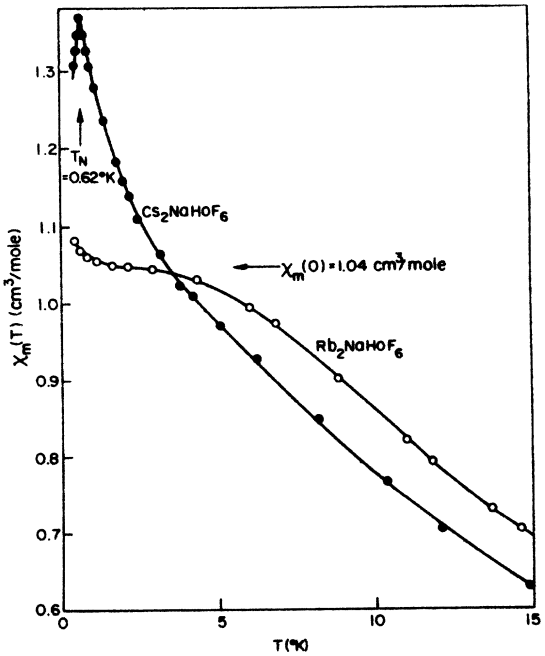

FIG. 4. Low-temperature susceptibility [(0.45–15)°K] of Rb_2NaHoF_6 and Cs_2NaHoF_6.

F. Rb_2NaHoF_6, Cs_2NaHoF_6

In octahedral point symmetry the ground state may be either Γ_1 or $\Gamma_3^{(2)}$.[30] For a certain ratio of fourth- to sixth-order crystal-field potential ($x = 0.857$)[30] we find accidental degeneracy between Γ_1, $\Gamma_3^{(2)}$, and $\Gamma_4^{(2)}$. Magnetically, the two Ho compounds behave quite differently, as shown in Fig. 4. Cs_2NaHoF_6 shows an antiferromagnetic transition at 0.62 K, whereas Rb_2NaHoF_6 shows Van Vleck paramagnetism. Most likely Cs_2NaHoF_6 is at or very near the point of accidental degeneracy.

From purely magnetic measurements alone, we cannot decide whether the magnetic transition in Cs_2NaHoF_6 is of pure exchange origin or whether it is at least partially hyperfine induced,[44,45] similar to $Ho_3Ga_5O_{12}$ (Ref. 46) and $Tb_3Ga_5O_{12}$.[46] Nonrelativistic and relativistic calculations yield $x = 0.884$ and 0.849, respectively, for $\xi = 0.275$, a value found for Cs_2NaErF_6.[20] For Rb_2NaHoF_6 we find $x = 0.866$ and 0.828 for $\xi = 0.265$. Usually sixth-order crystal-field potentials are always stronger than in the case of the EPCM. Therefore we tend to believe that the ground state in Rb_2NaHoF_6 is $\Gamma_3^{(2)}$ and that we are located at x values below 0.857. Because $\Gamma_3^{(2)}$ forms off-diagonal matrix elements with four different levels ($\Gamma_4^{(1)}$, $\Gamma_4^{(2)}$, $\Gamma_5^{(1)}$, $\Gamma_5^{(2)}$) we cannot derive splittings from the Van Vleck susceptibility. This would still be true if Γ_1 were the ground state because the latter also couples to $\Gamma_4^{(1)}$ and $\Gamma_4^{(2)}$. With a $\Gamma_3^{(2)}$ state lowest, we expect a Jahn-Teller transition to occur. Unfortunately, no direct or indirect evidence for such a transition at low temperature could be found.

Regardless of what the crystal-field ground state is, we can calculate the hyperfine enhancement factor for Ho^{165} and we find 138, a rather large value. The Ho nuclear susceptibility is detectable below 1 K and appears superposed on the Van Vleck susceptibility, as shown in Figs. 4 and 5. We can measure the hyperfine enhancement factor $(1+K)$ directly from the relation[7]

$$\chi = \chi_{4f}(0) = g_N^2 \mu_N^2 I(I+1)(1+K)^2/3kT, \qquad (6)$$

neglecting nuclear-nuclear exchange. For Ho^{165} ($I = \frac{7}{2}$ and $\mu = 4.12\mu_N$) we find from (6), $1+K = 140 \pm 5$, in good agreement with a theoretical value of 138. Several demagnetization runs were tried from various starting temperatures and fields. Unfortunately, at temperatures below about 40 mK the Ho^{3+} nuclear system decouples thermally from the environment and it is difficult to test (6) to the millidegree range and to evaluate a possible temperature of the Ho^{165} nuclear system. In all cases, however, the residual en-

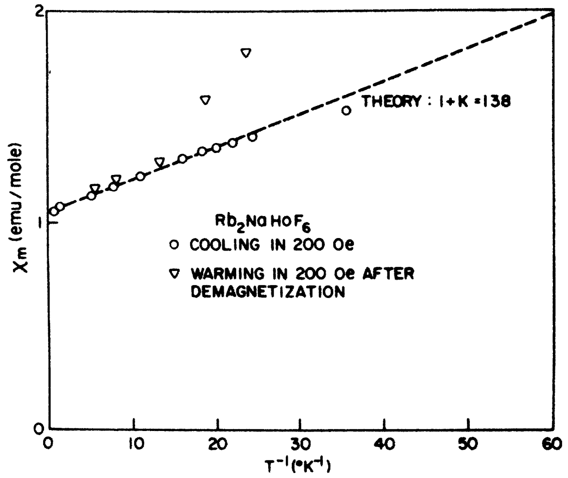

FIG. 5. Very-low-temperature susceptibility ((<1°K) of Rb_2NaHoF_6 vs T^{-1}.

hanced nuclear moment χH_r (where H_r is the residual field after demagnetization) was constant and about 850 emu/mole.

To second order, the hyperfine admixture of $4f$ angular momentum[7] to the nuclear substates in the Van Vleck ground state is $\langle J\rangle = (g_N\mu_N/g_J\mu_B)KI$. For complete nuclear polarization (100%) one would expect a saturation moment (per mole) of magnitude $m_s = Lg_N\mu_N I(K+1) = 1730$ emu/mole. This indicates that our demagnetization experiments were done with about 50% nuclear polarization. If (6) remained valid at very low temperatures it means a nuclear Ho spin temperature of about 2.5 mK was reached after demagnetization down to $H_r = 135$ Oe. However, especially in view of the possible Γ_3 doublet ground state, the degeneracy of which must be removed somewhere, (6) is probably no longer valid at these temperatures and we therefore do not know the true temperature after demagnetization.

G. Rb_2NaErF_6, $Rb_2NaY_{0.9}Er_{0.1}F_6$, Rb_2NaYbF_6

In Table I we have also studied a few other non-Kramers ions besides Gd. The level system of Er^{3+} is too complex and no crystal-field splittings from the temperature dependence of χ can be derived. In general splittings are not very accurate if derived from $\chi(T)$ and we will not pursue this problem further. Rb_2NaYbF_6 has recently been studied by Mössbauer effect and it was demonstrated that Γ_6 is indeed the ground state[47] as expected from a negative-ligand charge model.[30] None of the other Kramers systems appear to order magnetically above 0.45 K.

Note added in proof. A similar study was recently conducted on the Cs_2NaRCl_6 series by M. V. Hoehn and D. G. Karraker, J. Chem. Phys. 60, 393 (1974). Their results are very similar to ours, except that crystal-field splittings are smaller in the chlorides.

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