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Adiabatic Demagnetization of Cobaltous Fluosilicate

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The adiabatic demagnetization experiment has been carried out on a single crystal of cobaltous fluosilicate for the directions parallel and perpendicular to the c-axis. Instead of ordinary susceptibility measurement the static magnetization curves were measured in a wide field region with a recording fluxmeter. From the isothermal magnetization curves g-values were obtained ($g_{\parallel}=7.27$, $g_{\perp}=2.28$). The adiabatic magnetization curves were obtained for several entropy values. From the comparison of the estimated adiabatic magnetization curves at zero entropy with the molecular field theory of antiferromagnetism, it was concluded that the magnetic behavior of this substance is the same as in the case of antiferromagnetism with the prefered axis along the c-axis. The Néel temperature was determined to be about 0.15°K. For the direction perpendicular to the c-axis, there appeared a weak ferromagnetism of 3.5% with hysteresis loop. This weak ferromagnetism may be related to the crystal structure of the low temperature modification.

The ground state of the Co^{2+} ion in $Co(H_2O)_6 \cdot SiF_6$ at liquid helium temperatures can be described by an effective spin $S'=\frac{1}{2}$, and its g-values are highly anisotropic[1] between the direction along the trigonal field of water octahedron and the direction perpendicular to it. The exchange interaction is dominant in comparison with the dipole-dipole interaction[2], and the exchange interaction is thought to be strong along the c-axis due to the hydrogen bond structure. The trigonal crystalline field axis coincides with the c-axis. It would be of interest to observe the magnetic ordering in this substance below 1°K.

The single crystal specimen was ball shaped about 12 mm in diameter. Magnetization curves were measured with a recording fluxmeter.

A search coil and a fully compensating coil are placed in the center of the magnet, and so the resultant electromotive force in two coils is due to the magnetization change of the specimen in the search coil. The magnetization can be obtained by integrating this electromotive force.

The field value which comes from the Hall voltage of the germanium crystal attached on the pole face is recorded simultaneously with the magnetization value on an XY-recorder. By this method it has been possible to measure the static magnetization curve in a wide field region. Heat influx into the specimen through the leads is reduced by winding the wires on the liquid helium container and by embedding the wires in a "heat guard" of powdered Mn Tutton salt cast with resin.

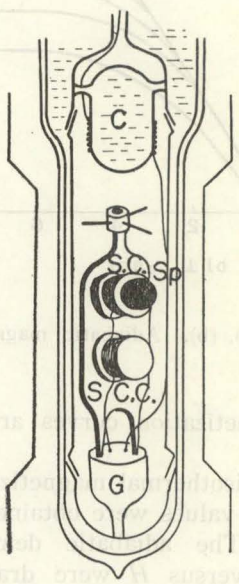

Fig. 1. Cryostat and search coil system. C: Liquid helium container. S. C.: Search coil, 400 turns. Sp: Specimen, 12mm in diameter. C. C.: Compensating coil. S: support for coils. G: "Heat guard", powdered Mn Tutton salt cast in a cold-setting resin.

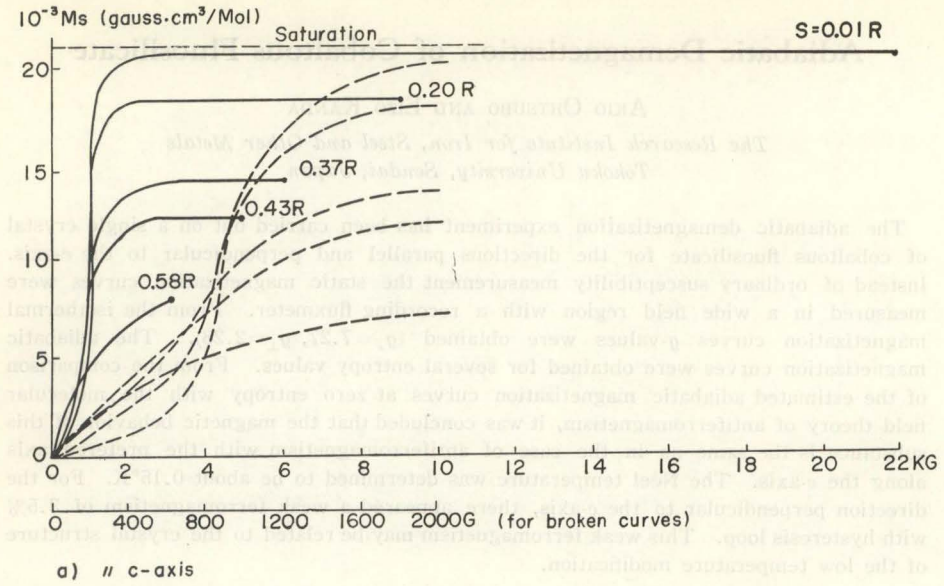

Fig. 2. (a)

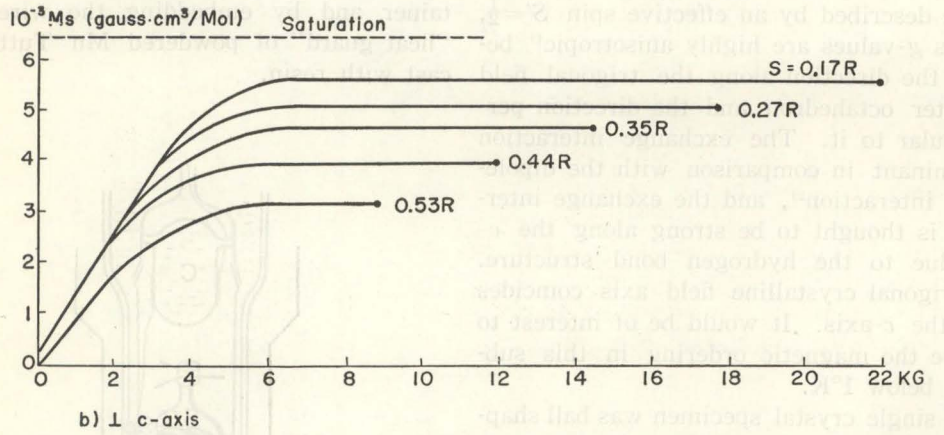

Fig. 2 (b)

Fig. 2. (a), (b). Adiabatic magnetization curves. Broken curves are drawn in enlarged field scale.

The magnetization curves are shown in Fig. 2.

From the isothermal magnetization curves at 1.05°K, g-values were obtained. ($g_{\parallel}=7.27$, $g_{\perp}=2.28$). The adiabatic demagnetization curves M_s versus H were drawn directly from an initial field down to zero through an adiabatic demagnetization process in about 15 seconds. The flat parts of the adiabatic magnetization curves correspond to the paramagnetic region. At the low field the adiabatic magnetization M_s decreases due to the phase transition into some antiferromagnetic state.

The magnetic behavior in this region is of a typical antiferromagnetic character. To go into more detail, we will try to use the result of the molecular field theory of antiferromagnetism. The most simple case of the molecular field theory is the isothermal magnetization curve at 0°K.

The magnetic property at 0°K is equivalent to that in the state of zero entropy, because in both states all the spins populate the lowest energy level. Now suppose the estimated adiabatic magnetization curve at

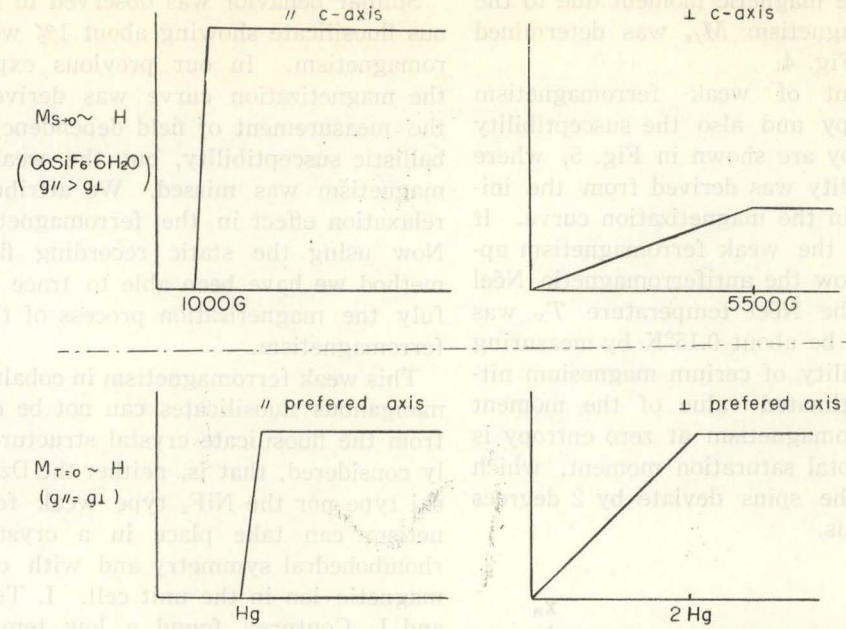

Fig. 3. The adiabatic magnetization curves of this substance at zero entropy in comparison with the isothermal magnetization curves at 0°K derived from the molecular field theory of the antiferromagnetism with isotropic g-value.

zero entropy obtained by extrapolating the curves at various entropy values to the limiting case of zero entropy. (Fig. 3)

The curve for each direction parallel or perpendicular to the c-axis can be compared directly with the isothermal magnetization curve at 0°K derived from the molecular field theory of antiferromagnetism.

In the adiabatic magnetization curve at zero entropy for the direction along the c-axis, there is a sudden change of magnetization from 0 to the saturation value at about 1000 gauss. For the direction perpendicular to it, the magnetization increases in proportion to field and at about 5500 gauss it reaches the saturation value.

These behaviors are just the same as in the case of the antiferromagnetism with the prefered axis along the c-axis having much larger anisotropy field than exchange molecular field. The spin flopping which occurs in the case with a small anisotropy field does not appear along this preferred axis, because $g_{\parallel}$ is very much larger than $g_{\perp}$. There are some differences between this real case and the simple theoretical case with isotropic g-value.

This difference is due to the large anisotropy of g-values in this salt. The saturation moment for each direction is different and is proportional to each g-value. The ratio of the saturation fields for the directions perpendicular and parallel to the c-axis should not be 2, but $2\times g_{\parallel}/g_{\perp}$. The ratio of the real case $5500G/1000G$ is nearly equal to $2\times 7.27/2.28$.

For the direction perpendicular to the c-axis, there appeared a weak ferromagnetism showing abrupt change of magnetization near zero field. (Fig. 2,b). By enlarging the scale in the X-Y recorder, hysteresis loops were

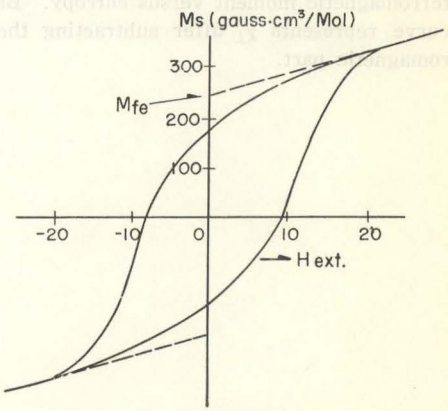

Fig. 4. Hysteresis loop perpendicular to c-axis, $S=0.17R$.

observed. The magnetic moment due to the weak ferromagnetism M_{fe} was determined as shown in Fig. 4.

The moment of weak ferromagnetism against entropy and also the susceptibility against entropy are shown in Fig. 5, where the susceptibility was derived from the initial gradient in the magnetization curve. It is clear that the weak ferromagnetism appears just below the antiferromagnetic Néel point T_N. The Néel temperature T_N was determined to be about 0.15°K by measuring the susceptibility of cerium magnesium nitrate. The estimated value of the moment of weak ferromagnetism at zero entropy is 3.5% of the total saturation moment, which means that the spins deviate by 2 degrees from the c-axis.

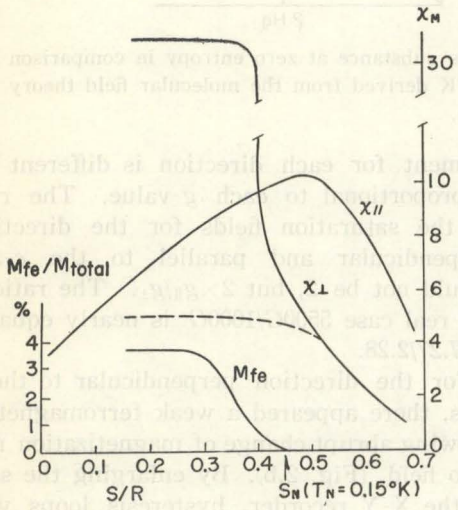

Fig. 5. Susceptibility versus entropy and weak ferromagnetic moment versus entropy. Broken curve represents $\chi_\perp$ after subtracting the ferromagnetic part.

Similar behavior was observed in manganous fluosilicate showing about 1% weak ferromagnetism. In our previous experiment the magnetization curve was derived from the measurement of field dependency of the ballistic susceptibility, but the weak ferromagnetism was missed. We attribute it to relaxation effect in the ferromagnetic part. Now using the static recording fluxmeter method we have been able to trace successfuly the magnetization process of the weak ferromagnetism.

This weak ferromagnetism in cobaltous and manganous fluosilicates can not be expected from the fluosilicate crystal structure usually considered, that is, neither the Dzialoshinski type nor the NiF_2 type weak ferromagnetism can take place in a crystal with rhombohedral symmetry and with only one magnetic ion in the unit cell. I. Tsujikawa and L. Couture[3] found a low temperature modification in manganous and cobaltous fluosilicates by optical observation. On cooling at about −50°C the whole single crystal with rhombohedral symmetry shattered into many column crystallites with the lower symmetry. The weak ferromagnetism may be related to the crystal structure of this modification. The crystal structure analysis of this modification is desirable.

References

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2 R. J. Benzie, A. H. Cooke and S. Whitley: Proc. Roy. Soc. **A232** (1955) 277; magnetic specific heat, $C_mT^2/R=16.1\times10^{-3}$ (exchange) + 1.2×10^{-3} (dipole)+1.2×10^{-3} (h.f.s.) deg².

3 I. Tsujikawa and L. Couture: J. de Phys. Rad. **16** (1955) 430; and private communication.