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Magnetic phase transitions in anisotropic Heisenberg antiferromagnets. II. $CoCl_2 \cdot 6H_2O$†

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Differential magnetic susceptibility measurements have been used to examine the temperature dependence of the magnetic phase boundaries in antiferromagnetic $CoCl_2 \cdot 6H_2O$ between 0.33 and 2.0 K. The spin-flop to paramagnetic phase boundary has a predominantly $T^{5/2}$ temperature dependence, similar to the case of $MnCl_2 \cdot 4H_2O$ reported in the preceding paper. No evidence is found for the predicted $T^{3/2}$ dependence. The values of the critical fields, extrapolated to $T = 0$, are consistent with a Heisenberg model with isotropic exchange and a single-ion-type anisotropy.

I. INTRODUCTION

In the preceding paper (I) the observed magnetic phase transitions in $MnCl_2 \cdot 4H_2O$ were discussed and the results compared with spin-wave and mean-field theory. A rather serious discrepancy exists between the observed and predicted temperature dependence of the phase boundaries bordering the paramagnetic (P) state at low temperatures. In view of the fact that the predicted behavior is based on the well-founded theory of antiferromagnetic spin-wave renormalization of Anderson and Callen,[1] it seemed desirable to test the comparison between experiment and theory in a different antiferromagnetic compound, $CoCl_2 \cdot 6H_2O$.

$CoCl_2 \cdot 6H_2O$ exhibits rather simple antiferromagnetic order below $T_N = 2.29$ K. There is a well-defined spin-flop (SF) state separating the antiferromagnetic (AF) state and the P state below the bicritical point ($\simeq 2.05$ K). The unit cell is monoclinic with the angle $\beta = 122.33°$. An extensive x-ray study of the crystal structure was reported by Mizuno.[2] The magnetic structure was investigated by proton resonance studies by Spence *et al.*,[3] and by neutron diffraction by Kleinberg.[4] The preferred direction for magnetic spin alignment is the crystallographic c axis. The low-field phase transitions have been studied above 1.0 K by Van der Lugt and Poulis,[5] Schmidt and Friedberg,[6] and McElearney *et al.*[7] More recently, Metselaar and DeKlerk[8] measured the differential magnetic susceptibility in fields up to 60 kOe, from which the H-T phase diagram was determined above 1.2 K for the field along the c axis.

We have determined the phase boundaries down to 0.3 K from differential susceptibility measurements with the field along the c axis and the b axis. From these data it is possible to examine the low-temperature behavior of the phase boundaries for comparison with spin-wave theory.

II. EXPERIMENTAL PROCEDURE

Single crystals of $CoCl_2 \cdot 6H_2O$ were grown from saturated solution at room temperature by slow evaporation. A spherical sample was cut from a large single crystal and treated against water loss in the same manner as described in paper I. The experimental setup was identical to that described in paper I. Since the prime interest in this experiment was to locate the phase boundaries, the susceptibility was measured only in the vicinity of the phase transitions. The field dependence of the susceptibility had the same general features as that of $MnCl_2 \cdot 4H_2O$, except that the small peak at the SF-to-P transition was more pronounced.

III. RESULTS AND ANALYSIS

The critical fields for the phase transitions are determined from the susceptibility measurements taken at a series of temperatures with the field alternately along the c axis and the b axis. The resulting H-T phase diagram is shown in Fig. 1. Also shown for comparison are the data of Van der Lugt,[5] and Metselaar and DeKlerk[8] for the field along the c axis. The fields for the present data have been corrected for demagnetization effects. The data are tabulated in Table I.

A. Temperature dependence of the phase boundaries

From the theory of Anderson and Callen[1] we expect the temperature dependence of the SF-to-P phase boundary to be of the form (see paper I)

$$H_{\parallel}^{c}(T) = H_{\parallel}^{c}(0)(1 - C_1 T^{3/2} - C_2 T^{5/2}) , \qquad (1)$$

where the notation is the same as that used in paper I. For comparison to the data, we again rewrite Eq. (1) in the form

$$\Delta H_{\parallel}^{c}/H_{\parallel}^{c}(0)\, T^{3/2} = [H_{\parallel}^{c}(0) - H_{\parallel}^{c}(T)]/H_{\parallel}^{c}(0)\, T^{3/2} = C_1 + C_2 T . \qquad (2)$$

In Fig. 2 we show the data for $CoCl_2 \cdot 6H_2O$ where we have included the data for the AF-to-P transition which occurs with the field along the b axis. The solid lines are the best linear fits to the data, which yield $C_1 = 0.000$ for both phase boundaries. The dashed line is the expected behavior from the theory of Anderson and Callen[1] ap-

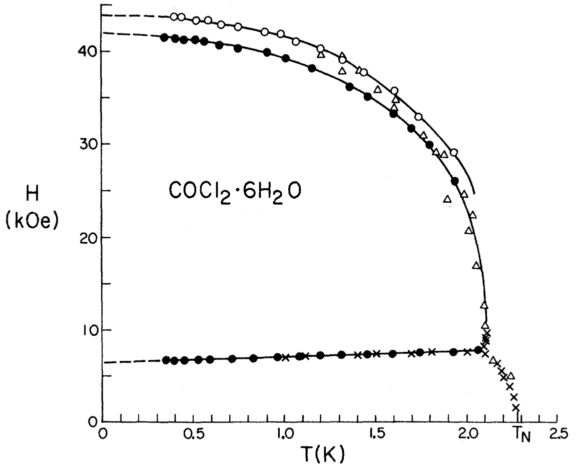

FIG. 1. H–T phase diagram for $CoCl_2 \cdot 6H_2O$. ●, present data for H along the c axis; ○, present data for H along the b axis; ×, data of Van der Lugt and Poulis (Ref. 5); △, data of Metselaar and DeKlerk (Ref. 8).

plied to $CoCl_2 \cdot 6H_2O$. The values of the critical fields at $T=0$ that were obtained from the fitting procedure are

$$H^c_\parallel(0) = 41.15 \pm 0.05 \text{ kOe}$$

and

$$H^c_\perp(0) = 43.20 \pm 0.05 \text{ kOe} .$$

The data at the higher temperatures show evidence of higher-order contributions. Assuming C_1 is identically zero we can check for higher-order terms by plotting $\Delta H^c/H^c(0)T^{5/2}$ against T. The results are shown in Fig. 3, where the best fits to the data are consistent with a small $T^{7/2}$ contribution. The values of the coefficients obtained from the data are tabulated in Table II along with the calculated values from the theories of Anderson and Callen[1] and Feder and Pytte.[9]

TABLE I. Critical internal fields for $CoCl_2 \cdot 6H_2O$.

	$\vec{H} \parallel \vec{c}$				$\vec{H} \parallel \vec{b}$
	AF - SF		SF - P		AF - P
T (K)	H_{c1} (kOe)	T (K)	H_{c2} (kOe)	T (K)	H_{cb} (kOe)
0.00	6.58[a]	0.00	41.15[a]	0.00	43.20[a]
0.352	6.68	0.332	40.99	0.388	43.05
0.391	6.68	0.365	40.99	0.426	43.05
0.440	6.72	0.447	40.82	0.514	42.71
0.529	6.76	0.514	40.65	0.567	42.71
0.591	6.79	0.567	40.65	0.638	42.36
0.712	6.88	0.638	40.31	0.738	42.02
0.818	6.96	0.738	39.96	0.892	41.51
0.957	7.01	0.892	39.45	0.972	41.34
1.083	7.08	1.014	38.77	1.064	40.65
1.194	7.14	1.151	37.74	1.189	39.97
1.310	7.31	1.353	35.85	1.307	38.60
1.440	7.41	1.447	34.83	1.433	37.22
1.593	7.53	1.587	32.941	1.593	35.171
1.740	7.63	1.688	31.402	1.729	32.432
1.918	7.76	1.795	29.524	1.918	28.666
		1.918	25.760		

[a] Extrapolated values.

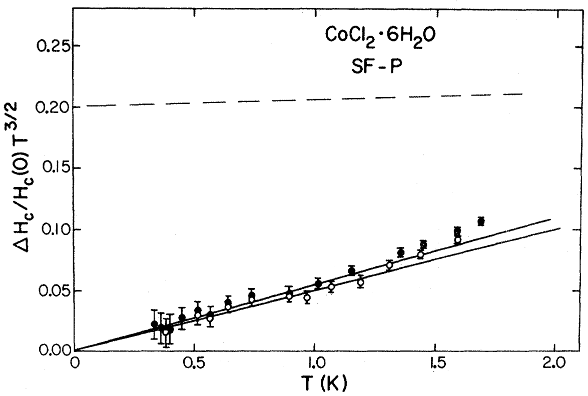

FIG. 2. Temperature dependence of the phase boundaries bordering the paramagnetic phase at low temperatures for $CoCl_2 \cdot 6H_2O$. ●, data for H along the c axis; ○, data for H along the b axis; solid line, best fit to the data; dashed line, theory of Anderson and Callen (Ref. 1).

The data for the AF-to-SF phase boundary are shown in Fig. 4, where we have plotted $\Delta H^{sf}_\parallel / H^{sf}_\parallel(0)T^{3/2}$ against T. The best fit to the data is shown by the solid line, which gives

$$H^{sf}_\parallel(T) = H^{sf}_\parallel(0)(1 + A\,T^{3/2}) ,$$

with

$$A = 0.070 \pm 0.007 \text{ K}^{-3/2}$$

and

$$H^{sf}_\parallel(0) = 6.58 \pm 0.01 \text{ kOe} .$$

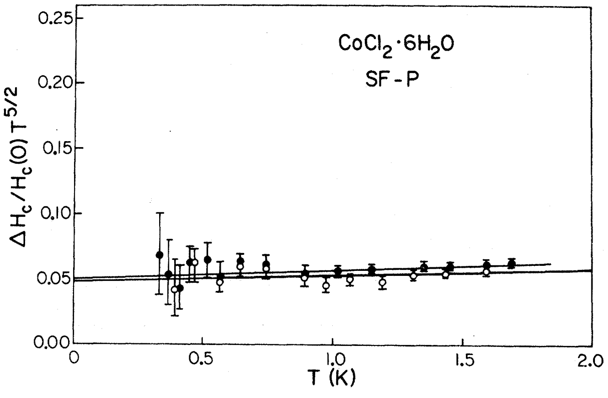

FIG. 3. Temperature dependence of the phase boundaries bordering the paramagnetic phase at low temperatures for $CoCl_2 \cdot 6H_2O$. ●, data for H along the c axis; ○, data for H along the b axis; solid line, best fit to the data.

From the theory of Feder and Pytte[9] for either uniaxial single-ion anisotropy or anisotropic exchange,

$$H_{\parallel}^{sf}(T) = H_{\parallel}^{sf}(0)(1 + \delta - AT^{3/2} + BT^{5/2}) , \qquad (3)$$

where $A = 0$ for anisotropic exchange, and δ is a small temperature-independent spin-wave correction. The data are not consistent with Eq. (3) for either type of anisotropy.

B. Exchange and anisotropy energies

Date[10] used a model including anisotropic exchange to explain the antiferromagnetic resonance data in $CoCl_2 \cdot 6H_2O$. On the other hand, Kimura[11] first considered uniaxial single-ion anisotropy in his investigation of the effect of the magnonphonon interaction on the specific heat. Later Kimura[12] extended these calculations to include anisotropic exchange; however, the earlier theory appeared to fit the data better. The temperature dependence of the AF-to-SF phase boundary discussed above gives no insight into the nature of the anisotropy, since it does not agree with the first-order spin-wave theory for either type of anisotropy.

The critical fields for the phase transitions are simply related to the effective exchange and anisotropy fields, as discussed in paper I. Including both types of anisotropy the critical fields can be expressed in the form

$$H_{\parallel}^{c}(0) = 2h_E + h_{AK} - h_{A1} , \qquad (4)$$

$$H_{\perp}^{c}(0) = 2h_E + h_{AK} + h_{A1} , \qquad (5)$$

and

$$H_{\parallel}^{sf}(0) = [(2h_E + h_{AK} + h_{A1})(h_{AK} + h_{A1})]^{1/2} , \qquad (6)$$

where h_E, h_{AK}, and h_{A1} are the effective isotropic exchange field, anisotropic exchange field, and single-ion anisotropy field, respectively. Putting the values of the critical fields obtained above in Eqs. (4)–(6) we obtain

$$h_E = 21.09 \pm 0.03 \text{ kOe} ,$$

$$h_{AK} = 0.00 \pm 0.02 \text{ kOe} ,$$

$$h_{A1} = 1.025 \pm 0.05 \text{ kOe} .$$

Analysis of the critical-field data, thus, leads to a negligible anisotropic exchange field and a relatively small single-ion anisotropy.

TABLE II. Comparison of theoretical and experimental critical-field parameters for $H^c = H^c(0)(1 - C_1 T^{3/2} - C_2 T^{5/2} - C_3 T^{7/2})$. SF-to-P transition and perpendicular AF-to-P transition in $CoCl_2 \cdot 6H_2O$.

	C_1	C_2	C_3
Theory			
AC (Ref. 1)	0.20	0.006	...
FP (Ref. 9)	0.20	...	...
Experimental			
c axis	0.000 ± 0.004	0.050 ± 0.006	0.007 ± 0.001
b axis	0.000 ± 0.004	0.048 ± 0.005	0.005 ± 0.001

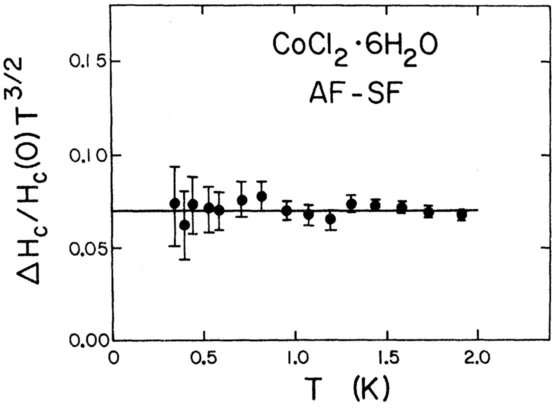

FIG. 4. Temperature dependence of the AF-to-SF phase boundary for $CoCl_2 \cdot 6H_2O$. ●, data; solid line, best fit to the data.

IV. DISCUSSION

The temperature dependence of the phase boundaries that border the paramagnetic state at low temperatures in $CoCl_2 \cdot 6H_2O$ shows no evidence for the predicted $T^{3/2}$ dependence. This fact, coupled with the identical result in $MnCl_2 \cdot 4H_2O$ reported in paper I, leads to the conclusion that the observed phase boundaries are not described properly by the first-order spin-wave theories of Anderson and Callen[1] and Feder and Pytte.[9] Since the first-order method that is used to treat spin-wave interactions is generally accepted as correct, one can conclude that, either the interactions must be treated to higher order, or there is a breakdown in the argument that the phase boundaries should exactly reflect the temperature dependence of the renormalized spin-wave energies.

The nature of the anisotropy in $CoCl_2 \cdot 6H_2O$ appears uncertain. The present work is consistent with a model of single-ion anisotropy, whereas, anisotropic exchange was used successfully by Date[10] to explain the antiferromagnetic resonance experiments. In the theory of Kimura[11,12] it is not clear what effect the particular model for anisotropy had on the calculated specific heat.

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[1] F. B. Anderson and H. B. Callen, Phys. Rev. 136, A1068 (1964).

[2] J. Mizuno, J. Phys. Soc. Jpn. 15, 1412 (1960).

[3] R. D. Spence, P. Middents, Z. El Saffar, and R. Kleinberg, J. Appl. Phys. 35, 854 (1964).

[4] R. Kleinberg, J. Chem. Phys. 53, 2660 (1970).

[5] W. Van der Lugt and N. J. Poulis, Physica 26, 917 (1960).

[6] V. A. Schmidt and S. A. Friedberg, J. Appl. Phys. 38, 5319 (1967).

[7] J. N. McElearney, H. Forstat, and P. T. Bailey, Phys. Rev. 181, 887 (1969).

[8] J. W. Metselaar and D. DeKlerk, Physica 63, 191 (1973).

[9] J. Feder and E. Pytte, Phys. Rev. 168, 640 (1968).

[10] M. Date, J. Phys. Soc. Jpn. 16, 1337 (1961).

[11] I. Kimura, J. Phys. Soc. Jpn. 28, 1182 (1970).

[12] I. Kimura, J. Phys. Soc. Jpn. 33, 6 (1972).