PHYSICAL REVIEW B VOLUME 21, NUMBER 9 1 MAY 1980

Intermediate phase in the spin-flop system $CoBr_2 \cdot 6(0.48D_2O, 0.52H_2O)$

J. A. J. Basten* and W. J. M. de Jonge
Department of Physics, Eindhoven University of Technology,
5600 MB Eindhoven, The Netherlands

E. Frikkee
Netherlands Energy Research Foundation ECN,
1755 ZG Petten (N.H.), The Netherlands

(Received 23 October 1979)

In the weakly anisotropic antiferromagnet $CoBr_2 \cdot 6(0.48D_2O, 0.52H_2O)$ the reorientation of the sublattice magnetizations from antiferromagnetic (AF) to spin-flop (SF) ordering has been studied by neutron scattering and magnetization measurements. Strong evidence has been obtained for the existence of an intermediate phase between the AF and SF phase, which persists up to a tetracritical point.

In the magnetic phase diagrams of weakly anisotropic antiferromagnets determined thus far, the transition from the antiferromagnetic (AF) to the spin-flop (SF) phase, due to an increasing magnetic field applied along the easy axis of the system, has been reported to be of first order. However, several theoretical calculations, mainly in the molecular-field (MF) approximation,[1,2] indicate that for certain combinations of the inter- and intrasublattice interaction parameters an intermediate (I) phase may exist between the AF and SF phases, separated from these by second-order phase boundaries.

Here we shall report a study on $CoBr_2 \cdot 6(0.48D_2O, 0.52H_2O)$, further denoted as CB48, in which the reorientation of the sublattice magnetizations from the AF to the SF ordering has been observed by neutron scattering (NS) and magnetization measurements. It appears that this reorientation extends over an anomalously wide field range, which cannot be caused by a first-order spin-flop transition, but, as we shall show, can be very well accounted for by the existence of an I phase. To our knowledge this is the first time that the existence of an I phase in a one-component spin-flop system is reported.

In the MF approximation the Gibbs free energy of a two-sublattice antiferromagnet in a magnetic field can be expressed as[1]

$$G = \frac{2}{N\mu^2} \sum_{i=\alpha,\beta,\gamma} \{A_i M_i^A M_i^B - \tfrac{1}{2} D_i [(M_i^A)^2 + (M_i^B)^2]\} + \sum_{i=\alpha,\beta,\gamma} H_i (M_i^A + M_i^B) \quad , \qquad (1)$$

where $\vec{M}^A$ and $\vec{M}^B$ are the sublattice magnetizations, A_i and D_i represent the i component of the inter- and intrasublattice couplings, respectively, and μ is the magnetic moment of the magnetic ions. α, β, and γ indicate the hard, intermediate, and easy axes, respectively. It has been shown[1,2] that in antiferromagnets with $A_i > 0$ for all i, four thermodynamically stable phases can exist in an applied magnetic field H_γ along the easy axis. In addition to the familiar AF, SF, and paramagnetic (P) phases, a stable I phase can exist between the AF and the SF phase, if $\Delta < 0 < A_\beta < A_\gamma + \Delta$, where $\Delta \equiv D_\gamma - D_\beta$. The condition $\Delta < 0$ implies that the anisotropy in D would favor moment alignment along β. The I phase is characterized by a gradual rotation of the staggered magnetization $\vec{M}_{st} \equiv \vec{M}^A - \vec{M}^B$ from the γ axis to the β axis with increasing H_γ. Possible sequences of stable phases with increasing H_γ are shown in Fig. 1.

The structure of $CoBr_2 \cdot 6[xD_2O, (1-x)H_2O]$ is monoclinic (space group $C2/m$) for $x < 0.55$, whereas for $x > 0.55$ a transition occurs from this monoclinic to a triclinic structure (space group $P\bar{1}$) at

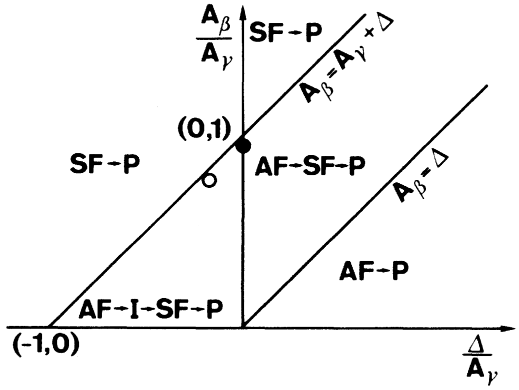

FIG. 1. Sequences of thermodynamically stable solutions in increasing field H_γ, for different combinations of MF constants at $T=0$ (taken from Ref. 1). The locations of CB48(○) and $CoBr_2 \cdot 6H_2O$(●) are indicated.

low temperatures.[3,4] The symmetry of the AF ordering, taking place below $T_N \approx 3.1$ K for all x, is described by the magnetic space group $C_{2c}2'/m'$ for $x < 0.55$. The easy γ axis is located in the ac mirror plane for symmetry reasons and makes an angle of 8° with the c axis towards the c^* axis.[5] For $x > 0.55$ the magnetic space group is $P_{2a}\bar{1}$, and the easy axis is rotated out of the ac plane.[4] In the monoclinic compounds, the application of a magnetic field $H_\gamma \gtrsim 7.5$ kOe (at $T=0$) parallel to the γ axis brings the system in the SF phase, where the moments are directed approximately along the intermediate β axis (i.e., the monoclinic b axis).[6]

The CB48 sample used in the NS experiment was a large single crystal of $2 \times 1.5 \times 0.5$ cm^3, shaped roughly ellipsoidal to reduce inhomogeneities in the demagnetizing field. For the magnetization measurements small crystals were selected from the same batch. In order to check on the crystallography of the samples, another part of the batch was used to record a neutron-diffraction powder diagram at 4.2 K. From the standard profile analysis the anticipated $C2/m$ structure was confirmed and the deuterium fraction was determined as $x = 0.483(8)$.

The NS experiment on the phase transition of CB48 was performed on a double-axis diffractometer at the Petten research reactor. The sample was fixed with the b axis vertical in a liquid-helium bath cryostat, which was mounted on a conventional magnet with $\vec{H}$ horizontal (inhomogeneity over the sample <0.5%). Special care was taken to achieve an accurate horizontal alignment of the easy-hard (ac) plane, by maximizing the intensities of several sets of Bragg reflections in presence of 10′ vertical collimation in front of and behind the sample. From this procedure and possible imperfections in the construction of the diffractometer, the alignment of $\vec{H}$ with respect to the ac plane was estimated to be correct within 7′, which is comparable with the 8′ full width at half maximum mosaic spread of the crystal. Within the ac plane optimum orientation of $\vec{H}$ along the γ axis could be obtained, by rotating $\vec{H}$ with respect to the sample. The magnetization measurements were performed in a standard Foner magnetometer, in which the crystals could be oriented within approximately 0.5° with respect to $\vec{H}$.

In NS experiments, the variation in the order parameters of the AF phase (i.e., $M_{\rm st}^{\parallel} \equiv M_{\rm st}^{\gamma}$) and of the SF phase (i.e., $M_{\rm st}^{\perp} \equiv M_{\rm st}^{\beta}$) can be derived from the intensity variations of the magnetic Bragg reflections. In the experiment on CB48 we have recorded the peak intensity of the $(10\frac{3}{2})$ reflection at several temperatures with increasing H_γ. A typical example at $T \ll T_N$ is shown in Fig. 2. In the AF phase ($H < H_{\rm IA}$) the intensity hardly exceeds the background, since the angle between the γ direction and the reciprocal-lattice vector $(10\frac{3}{2})$ is only 3.2°.[7] In the SF phase ($H > H_{\rm IS}$) the intensity $I \propto (M_{\rm st}^{\perp})^2$ does not vary very much up to the maximum applied field of 15 kOe, which is much lower than the saturation field $H_c \approx 54$ kOe (at $T=0$). Between $H_{\rm IA}$ and $H_{\rm IS}$ a *linear increase* in intensity is observed. If the transition is of first order, a linear increase results from the formation of domains.[8] However, the maximum field range for such a transition can be calculated[9] as $\Delta H_{\max} = 4\pi\chi_\perp H_{\rm SF}$. With $\chi_\perp$ taken from Ref. 5 and the spin-flop field $H_{\rm SF} \approx 8$ kOe we find for CB48 the value $\Delta H_{\max} \approx 160$ Oe. The anomalously broad transition range $\Delta H = H_{\rm IS} - H_{\rm IA} \approx 1500$ Oe was confirmed by the observed variation of the magnetization M_γ at $T = 1.2$ K, shown in Fig. 3(a). With the misalignment estimated as $\psi \lesssim 0.5°$, M_γ varies largely linearly in the range $H_{\rm IS} - H_{\rm IA} \approx 1800$ Oe.

Frequently, such a broadened transition is due to a misalignment between $\vec{H}$ and the easy-hard plane. If the misalignment angle ψ exceeds a critical angle $\psi_c(T)$, corresponding to the edge of the first-order spin-flop shelf,[10] one will observe a gradual rotation of $\vec{M}_{\rm st}$ towards the intermediate axis over a broadened field range. If $\psi \gg \psi_c$ this rotation can be described by the MF expression[11]

$$\tan(2\zeta + 2\psi) = \sin 2\psi / (\cos 2\psi - H^2/H_{\rm SF}^2) \quad , \qquad (2)$$

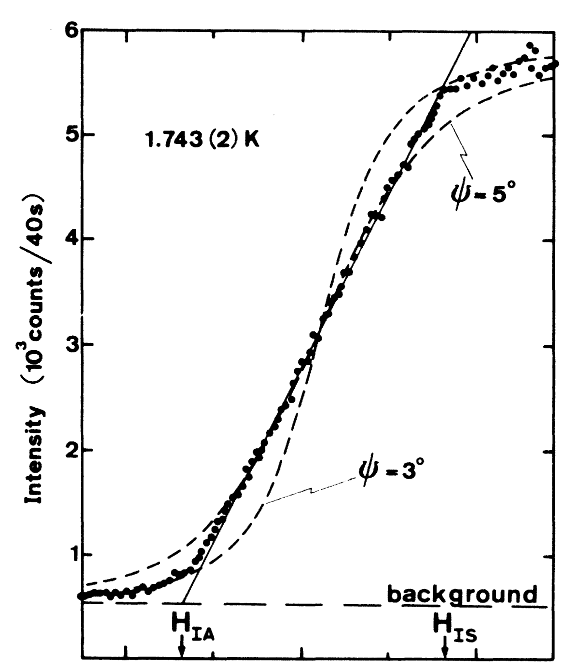

FIG. 2. Field scan of the peak intensity of the $(10\frac{3}{2})$ reflection compared with the theoretical prediction for a broadened first-order transition: $I \propto \sin^2\zeta(H)$, where $\zeta(H)$ is calculated from Eq. (2) for two values of the misalignment angle ψ.

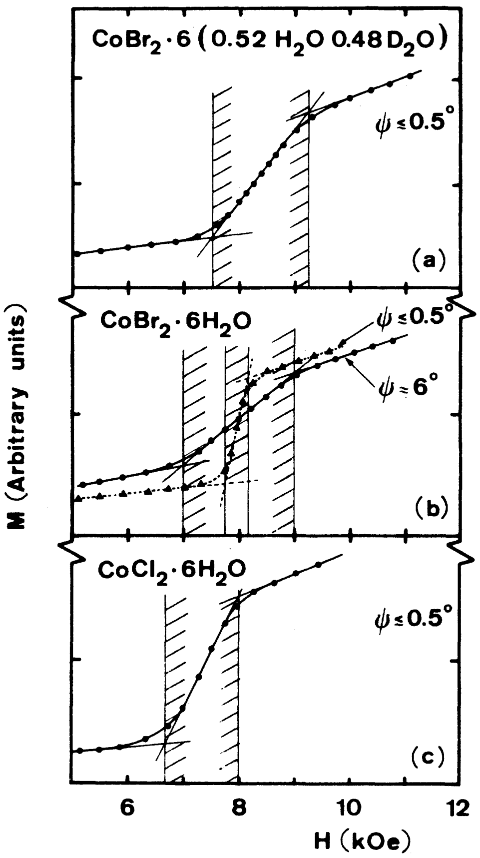

FIG. 3. Magnetization M vs H at $T=1.2$ K in the compounds (a) CB48, (b) $CoBr_2\cdot 6H_2O$, with $\vec{H}$ aligned along the γ axis as well as possible ($\psi \lesssim 0.5°$) and misaligned by 6°, (c) $CoCl_2\cdot 6H_2O$.

where ζ is the angle between $\vec{M}_{st}$ and the γ axis. The effect of incorrect field alignment may be illustrated by magnetization measurements performed at $T=1.2$ K on the genuine spin-flop system $CoBr_2\cdot 6H_2O$, for which $\psi_c(T=1.2\text{ K})\approx 0.7°$ [see Fig. 3(b)]. The minimum width of the transition is only 400 Oe, which is compatible with the expected $\Delta H_{max}\approx 160$ Oe for a first-order AF-SF transition and a misalignment $\psi\approx 0.5°$. An intentional misorientation $\psi\approx 6°$ leads to a transition width $\Delta H\approx 2$ kOe, as shown in Fig. 3(b).

Obviously, the results in Figs. 2 and 3(a) cannot be explained in terms of such a broadened spin-flop transition, because in both experiments the field misalignment ($\psi\lesssim 0.25°$ and $\lesssim 0.5°$) is much smaller than the value ($\psi\approx 5°$ and $\approx 5.6°$) which must be assumed in Eq. (2) to account for the observed transition range ($\Delta H\approx 1.5$ and 1.8 kOe).

An alternative explanation for the anomalous width of the transition would be a spread in the spin-flop transition due to an inhomogeneous distribution of H_2O and D_2O in the sample, as H_{SF} is strongly x dependent for $x\gtrsim 0.55$.[3] We consider this explanation as extremely unlikely, since it requires local concentrations up to $x\approx 0.65$, which would induce local deviations of the easy axis up to $\approx 20°$ out of the ac plane.[3] This, however, would lead to clearly observable magnetic scattering at $H=0$ in the $(10\frac{\bar{3}}{2})$ reflection, in contradistinction to our observations. Moreover, such a distribution $H_{SF}(x)$ would not explain the linearity of the data in Figs. 2 and 3(a).

In view of the arguments given above, it is clear that the experimental data do not permit an interpretation in terms of a usual spin-flop transition. On the other hand, all available evidence points towards the existence of an I phase between H_{IA} and H_{IS} in CB48. Additional indications supporting this proposition are:

(i) The field range $H_{IA}-H_{IS}\approx 1.5$ kOe becomes quite acceptable. When the experimental values $H_{IA}=7.35$ kOe and $H_{IS}=8.95$ kOe at $T=1.743$ K (Fig. 2), and $H_c(1.743\text{ K})\approx 47.5$ kOe (taken from Ref. 6) are inserted in the theoretical expressions[1]

$$\mu H_{IA}=[(A_\gamma-A_\beta+\Delta)(A_\gamma+A_\beta+\Delta)]^{1/2}\ ,$$

$$\mu H_{IS}=(A_\gamma+A_\beta-\Delta)\times[(A_\gamma-A_\beta+\Delta)/(A_\gamma+A_\beta+\Delta)]^{1/2}\ ,$$

$$\mu H_c=(A_\gamma+A_\beta-\Delta)\ , \qquad (3)$$

we obtain $A_\beta/A_\gamma=0.77$, $\Delta/A_\gamma=-0.17$, and $A_\gamma=4.14$ K. These values may be compared with the reported values[12] for $CoBr_2\cdot 6H_2O$: $A_\beta/A_\gamma=0.95$, $D_\gamma/A_\gamma=-0.10$, and $A_\gamma=4.80$ K. In the diagram of Fig. 1, the locations of both CB48 and $CoBr_2\cdot 6H_2O$ are indicated, assuming the same anisotropy in D and A in the latter compound.

(ii) In the I phase, the MF theory[1] predicts indeed a *linear increase* with H_γ of the $(10\frac{\bar{3}}{2})$ intensity ($I\propto M_{st}^2\sin^2\zeta$) and the magnetization ($M_\gamma\propto|\vec{M}^A|\sin\zeta\sin\delta$, where δ is the angle between $\vec{M}^A$ and $\vec{M}_{st}$), in agreement with our observations [Figs. 2 and 3(a)].

There are indications that the existence of the I phase in CB48 may be related to the crystallographic instability of the system, which is a consequence of the proximity of the monoclinic-triclinic (m-t) transition at $x=0.55$ for low T.[3] In magnetization measurements on $CoCl_2\cdot 6H_2O$ the observed AF-SF transition is also unusually broad [see Fig. 3(c)], while the m-t transition in the partly deuterated system $CoCl_2\cdot 6[xD_2O(1-x)H_2O]$ takes place at $x=0.035$ for low T.[13] This observation of a broad transition in a pure system gives additional confidence that the observed effects in CB48 are of macroscopic origin and not due to an inhomogeneous distribution of D_2O and H_2O.

In conclusion it may be stated that the available experimental evidence is not compatible with the usual first-order spin-flop transition, but is in complete agreement with the existence of an I phase. NS results collected at a series of temperatures, show that this phase persists up to the tetracritical point $T_t = 2.82(2)$ K, $H_t = 9.2(2)$ kOe. It should be emphasized that in the present I phase the order parameters are *coupled,* in contrast to the I phase with decoupled order parameters observed in mixed magnetic compounds with competing spin anisotropies.[14,15] More detailed investigations are in progress.

---

[*] Present address: Dutch Metrological Service, Van Swinden Lab., P. O. Box 654, 2600 AR Delft, The Netherlands.

[1] Olga P. van Wier, Tineke van Peski-Tinbergen, and C. J. Gorter, Physica (Utrecht) 25, 116 (1959).

[2] K. S. Liu and M. E. Fisher, J. Low Temp. Phys. 10, 655 (1973).

[3] J. P. A. M. Hijmans, W. J. M. de Jonge, P. van der Leeden, and M. J. Steenland, Physica (Utrecht) 69, 76 (1973).

[4] J. A. J. Basten and A. L. M. Bongaarts, Phys. Rev. B 14, 2119 (1976).

[5] J. P. A. M. Hijmans, Q. A. G. van Vlimmeren, and W. J. M. de Jonge, Phys. Rev. B 12, 3859 (1975).

[6] J. W. Metselaar and D. de Klerk, Physica (Utrecht) 65, 208 (1973).

[7] J. A. J. Basten, in *Proceedings of a Symposium on Neutron Inelastic Scattering* (IAEA, Vienna, 1978), Vol. II, p. 247.

[8] See for instance, A. L. M. Bongaarts and W. J. M. de Jonge, Phys. Rev. B 15, 3424 (1977) (Appendix).

[9] A. R. King and D. Paquette, Phys. Rev. Lett. 30, 662 (1973).

[10] H. Rohrer and H. Thomas, J. Appl. Phys. 40, 1025 (1969).

[11] J. W. Lynn, P. Heller, and N. A. Lurie, Phys. Rev. B 16, 5032 (1977).

[12] K. Kopinga, P. W. M. Borm, and W. J. M. de Jonge, Phys. Rev. B 10, 4690 (1974).

[13] H. Benoit, W. Ghidalia, J. P. Legrand, and J. P. Renard, J. Phys. (Paris) 32, C1-1151 (1971).

[14] L. Bevaart, E. Frikkee, J. V. Lebesque, and L. J. de Jongh, Solid State Commun. 25, 539 (1978); L. Bevaart, E. Frikkee, and L. J. de Jongh, Phys. Rev. B 19, 4741 (1979).

[15] K. Katsumata, M. Kobayashi, T. Satō, and Y. Miyako, Phys. Rev. B 19, 2700 (1979); K. Katsumata, M. Kobayashi, and H. Yoshizawa, Phys. Rev. Lett. 43, 960 (1979).