Successive Ising phase transitions in a random antiferromagnet with competing anisotropies

K. Katsumata
Research Institute of Applied Electricity, Hokkaido University, Sapporo 060, Japan

H. Yoshizawa* and G. Shirane
Brookhaven National Laboratory, Upton, New York 11973

R. J. Birgeneau
Department of Physics, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139
(Received 9 August 1984)

We report the results of an elastic neutron scattering study of successive Ising phase transitions in the magnetic alloy $Fe_{0.4}Co_{0.6}Cl_2 \cdot 2H_2O$. Here the Fe^{2+} and Co^{2+} ions have orthogonal preferred spin directions so that this provides an example of a random magnet with competing anisotropies. The higher ($T_H = 11.8$ K) and the lower ($T_L = 6.15$ K) transition temperatures are equally sharp; furthermore, they both exhibit conventional critical scattering. These features are in contrast with those in all other competing anisotropy systems studied to date where the lower transitions are always broad and ill defined. Possible origins for the differing behavior in $Fe_{0.4}Co_{0.6}Cl_2 \cdot 2H_2O$ are discussed.

I. INTRODUCTION

Random magnetic systems continue to occupy the attentions of experimentalists and theorists alike.[1-3] One system which has received particular attention is a quenched magnetic binary alloy in which the constituent magnetic ions have orthogonal preferred spin directions.[4-11] In the idealized case that the Hamiltonian contains only diagonal interaction terms, it is expected that the ordering of the two orthogonal spin components should occur independently.[4,5] Thus the magnetic phase diagram in the concentration-temperature plane should consist of two second-order lines crossing each other smoothly at a point designated as a "decoupled tetracritical point."[5] For concentrations in the neighborhood of the tetracritical concentration there should then be successive second-order magnetic transitions with decreasing temperature in which one and then the other spin component achieves long-range order.

Phase diagrams having these general characteristics have now been observed in a number of binary alloys.[1] However, in only a few of these have the experiments been sufficiently precise that they allow a test of the above predictions for the idealized model. In each of $Fe_xCo_{1-x}Cl_2$,[7] $Co_{1-x}Fe_xTiO_3$,[8] and $K_2Co_xFe_{1-x}F_4$,[11] with the first having been most intensively investigated, it is found that the model Hamiltonian results do not hold. First, the phase transition lines do not appear to cross each other smoothly. Instead, especially in $Fe_xCo_{1-x}Cl_2$, there is a discontinuity in the slopes at the tetracritical point. Second, and more importantly, the lower transitions always appear to be appreciably rounded, in explicit disagreement with the predictions of a sharp second-order transition.[4,5] It is also found that for the species ordering at the lower temperature (labeled T_L) the associated spin correlations are anomalously long ranged between T_L and the higher transition temperature T_H. Wong *et al.*[7] have proposed that the rounding and the discontinuity in slope of the phase boundaries may be understood by considering the off-diagonal coupling terms omitted in the idealized theory. Such off-diagonal terms may arise from a variety of mechanisms, including anisotropic exchange, dipolar interactions, and magnetostriction effects.[12] Macroscopically, such off-diagonal interactions will average to zero by symmetry, but locally below T_H they give rise to a site random magnetic field.[2,3] It is now known that both discrete and continuous symmetry phase transitions are destroyed in three and fewer dimensions, provided that temperature is lowered in the presence of the random field.[2]

The one system which appears to exhibit behavior close to that expected for the idealized model is $Fe_{1-x}Co_xCl_2 \cdot 2H_2O$.[1,6] In this material the Fe^{2+} and Co^{2+} spins have orthogonal preferred spin directions; both having Ising symmetry so that this alloy provides an example of Ising-Ising tetracritical behavior. This contrasts with the compounds discussed above, all of which are Ising-XY type. The principal evidence for the sharpness of the lower-temperature transitions in $Fe_{1-x}Co_xCl_2 \cdot 2H_2O$ is a sharp feature observed at T_L in both specific-heat and susceptibility measurements.[6] In order to explore the ordering more thoroughly and to facilitate comparison with the other materials, especially $Fe_xCo_{1-x}Cl_2$, we have carried out a quasielastic neutron scattering study of one representative alloy, $Fe_{0.4}Co_{0.6}Cl_2 \cdot 2H_2O$. As we shall discuss, the behavior is indeed closer to that predicted by the idealized model,[5] suggesting that random-field effects are much less important in this system. Possible reasons for this will be discussed later.

The format of this paper is as follows. In Sec. II we present the relevant background information and details. The experimental results are given in Sec. III. A discussion and conclusions are given in Sec. IV.

II. PRELIMINARY DETAILS

The phase diagram of $Fe_{1-x}Co_xCl_2\cdot 2H_2O$ determined previously by Katsumata *et al.*[6] is shown in Fig. 1. Both $FeCl_2\cdot 2H_2O$ and $CoCl_2\cdot 2H_2O$ have the same monoclinic structure with the lattice parameters given in Table I; we also include the lattice parameters of the alloy studied here. The magnetic properties of $FeCl_2\cdot 2H_2O$ and $CoCl_2\cdot 2H_2O$ have been studied extensively[13–15] and are now well known. Both exhibit antiferromagnetism at low temperatures with identical ordered-state spin structures except for the spin directions. In $CoCl_2\cdot 2H_2O$, the spins point along the b axis orthogonal to the a-c plane. In $FeCl_2\cdot 2H_2O$ the spins are oriented along an axis which lies in the a-c plane and makes an angle of 32° with the c axis.[14,15] Thus the mixed crystal $Fe_{1-x}Co_xCl_2\cdot 2H_2O$ provides an example of a site random magnet with competing orthogonal Ising anisotropies. In the phase diagram, Fig. 1, the lines L_1 and L_4 indicate the ordering of the spin components in the a-c plane, while the lines L_2 and L_3 represent the ordering of the spin component along the b axis, which is the easy axis of $CoCl_2\cdot 2H_2O$. Mössbauer measurements[9] show that the Fe^{2+} spin has components along both directions in the mixed phase; presumably the same behavior holds for the Co^{2+} spin as well. It is evident that to within the uncertainties, the phase boundaries cross smoothly, as predicted by Fishman and Aharony.[5(b)]

The explicit sample studied here was a single-crystal parallelepiped with dimensions $7\times 7\times 30$ mm^3. The Fe concentration in the mother solution was 44 at. %; however, from the phase-transition temperatures determined in this study, we conclude that the actual concentration was closer to 40 at. %. We therefore label the compound $Fe_{0.4}Co_{0.6}Cl_2\cdot 2H_2O$. The material was in the form of a large single crystal with negligible mosaic spread, although there was a small ($\sim$2 vol %) twin separated in angle by $\sim$2.5°; the twin had no effect on any of the measurements reported here. From the magnetic Bragg scattering measurements near T_H, to be discussed in Sec. III, we estimate that the sample had a spread in concentration of $\Delta x = 0.007$ half-width at half maximum (HWHM).

TABLE I. Room-temperature lattice parameters.

	a (Å)	b (Å)	c (Å)	β
$FeCl_2\cdot 2H_2O$	7.355	8.548	3.637	98.2
$Fe_{0.4}Co_{0.6}Cl_2\cdot 2H_2O$	7.289	8.551	3.591	97.8
$CoCl_2\cdot 2H_2O$	7.256	8.575	3.554	97.5

The neutron scattering experiments were carried out using a triple-axis spectrometer at the Brookhaven High Flux Beam Reactor. The spectrometer was operated with an incident neutron energy of 14.4 or 30.5 meV obtained from the (002) reflection of a pyrolytic-graphite monochromator. Typically, we employed 20′ collimators throughout the instrument. Limited high-resolution measurements designed to eliminate double Bragg scattering were also carried out using 4-meV neutrons and 10′ collimators. The sample was mounted in a helium cryostat with the c axis vertical.

III. EXPERIMENTAL RESULTS

The experimental results may be described quite briefly. Our first measurements characterized the behavior of the magnetic Bragg scattering; the spectrometer was operated in a triple-axis mode with an incoming energy of 30.5 meV and the collimator configuration 20′-monochromator-20′-sample-20′-analyzer-40°-detector. The measured peak intensities as a function of temperature at (100) and (010) are shown in Figs. 2 and 3, respectively. The intensities are proportional to

$$M_b^2 + 0.718 M_a^2 \quad (100)$$

and (1)

$$M_a^2 \quad (010),$$

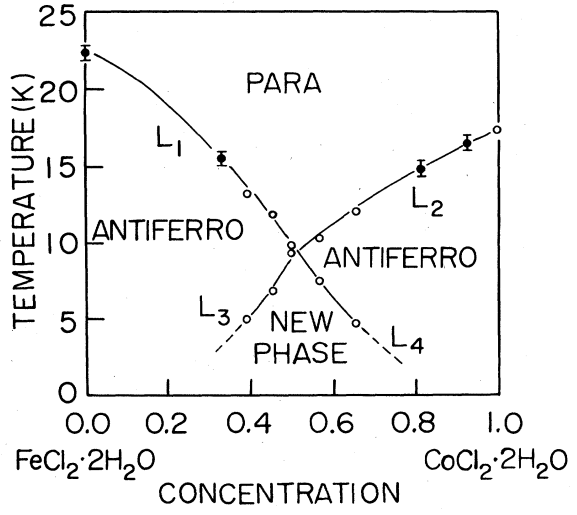

FIG. 1. Concentration versus transition-temperature phase diagram of $Fe_{1-x}Co_xCl_2\cdot 2H_2O$ obtained from measurements of specific heat (○) and susceptibility (●). Figure from Ref. 6.

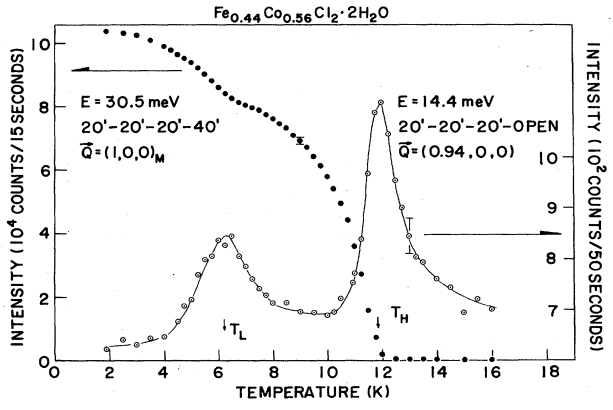

FIG. 2. Intensity of the (100) magnetic reflection in $Fe_{0.44}Co_{0.56}Cl_2\cdot 2H_2O$ plotted as a function of temperature. Also shown is the temperature dependence of the critical scattering at (0.9400); the respective spectrometer configurations are indicated in the figure.

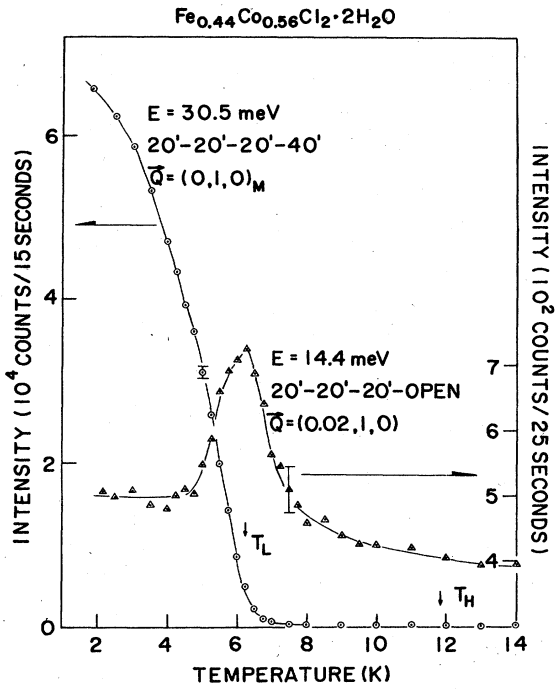

FIG. 3. Temperature dependences of the intensity of the (0 1 0) reflection and of the critical scattering at (0.02 1 0) for $Fe_{0.44}Co_{0.56}Cl_2 \cdot 2H_2O$; the respective spectrometer configurations are indicated in the figure.

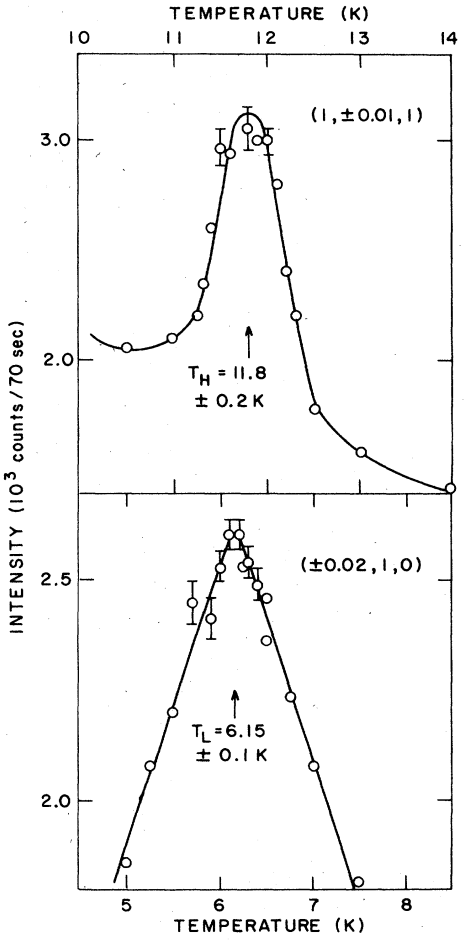

FIG. 4. High-statistics measurements of the peaks in the critical scattering at the indicated positions. The solid lines are guides to the eye.

where α is the preferred direction of $FeCl_2 \cdot 2H_2O$. In order to measure the associated peak in the critical scattering we switched to a double-axis configuration and lowered the neutron energy to 14.4 meV. The intensity was then measured as a function of temperature at a point slightly offset from the Bragg position. These results are also shown in Figs. 2 and 3. Higher-statistics measurements of the critical scattering in the immediate vicinity of the upper and lower transitions are shown in Fig. 4. These measurements were also carried out with a two-axis spectrometer with 20′ collimators and a neutron energy of 14 meV.

It is evident that the crystal $Fe_{0.4}Co_{0.6}Cl_2 \cdot 2H_2O$ exhibits its magnetic phase transitions of comparable sharpness at $T_H = 11.8 \pm 0.2$ K and at $T_L = 6.15 \pm 0.1$ K. On the intensity scale relevant to Fig. 3, there are no observable effects near 11.8 K at the $(0\,1\,0)_M$ position, whereas there is a sharp peak in both the critical scattering and the onset of magnetic Bragg scattering at $(1\,0\,0)_M$. From Eq. (1) this necessitates that only the b-axis component of the spins order at 11.8 K. The component in the a-c plane exhibits an independent transition at 6.15 K. It should be noted that we cannot determine the explicit spin direction of the component ordering at 6.15 K from these measurements alone, except to say that it lies in the a-c plane and that it must make an appreciable angle with the a^* direction; presumably it lies at least close to the preferred direction[14,15] in $FeCl_2 \cdot 2H_2O$.

In order to further test the decoupling of the spin components, we carried out some very-high-resolution measurements of the Bragg scattering at $(0\,1\,0)_M$; here we utilized a triple-axis spectrometer set for elastic scattering with 10′ collimators throughout and 4-meV neutrons. This configuration minimizes any contaminant processes such as double Bragg scattering. The results so obtained are shown in Fig. 5. It is evident that any Bragg scattering appearing below T_H must be at least 10^3 weaker than the Bragg scattering which appears below T_L.

Comparison of Figs. 2–5 with the corresponding figures (6–12) in the paper of Wong *et al.*[7] on $Fe_xCo_{1-x}Cl_2$ shows that the $Fe_{1-x}Co_xCl_2 \cdot 2H_2O$ system differs in an essential fashion from $Fe_xCo_{1-x}Cl_2$. In the former, both transitions are equally sharp and the order parameters are totally decoupled to within the experimental errors, whereas, as discussed previously, the lower-temperature transitions are severely rounded in the latter. An important difference also emerges when one examines the critical scattering associated with the lower-temperature transition. In $Fe_xCo_{1-x}Cl_2$ it is found that the critical scattering associated with T_L essentially has a resolution-limited width between T_L and T_H. In Fig. 6 we show transverse scans through (0 1 0) above T_L. The behavior

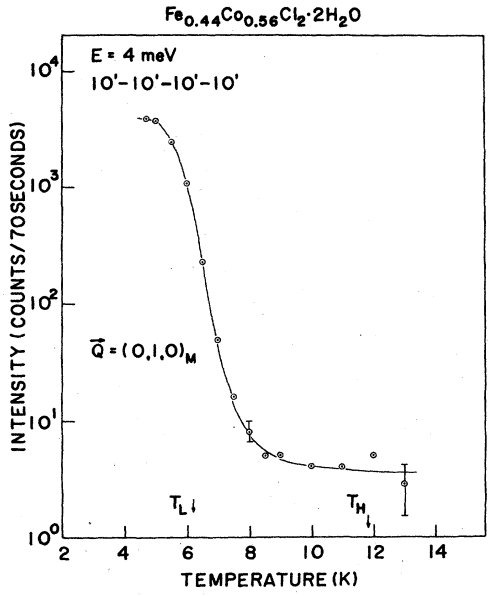

FIG. 5. Temperature dependence of the intensity of the (0 1 0) magnetic reflection for $Fe_{0.44}Co_{0.56}Cl_2 \cdot 2H_2O$ plotted on a logarithmic scale. The data points are the average over five to ten measurements and typical error bars are indicated.

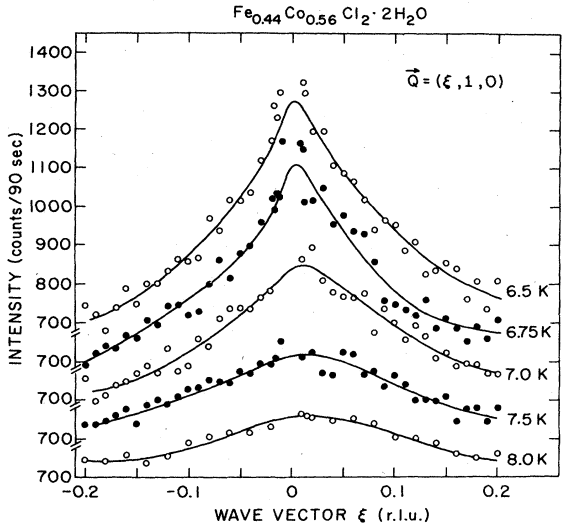

FIG. 6. Transverse scans of the critical scattering associated with the lower transition as functions of temperature above $T_L = 6.15$ K. The origins of the curves are displaced successively by 100 counts.

is entirely conventional. The inverse correlation length κ is ~ 0.2 reciprocal lattice units at 8 K and it decreases progressively as T_L is approached. Unfortunately, the concentration gradient precluded a proper study of the critical behavior in the immediate vicinity of T_L. Nevertheless, it is clear that there are no unusual features associated with the lower-temperature transition.

IV. DISCUSSION AND CONCLUSIONS

These experiments strongly support the previous deductions[1,6] that the $Fe_{1-x}Co_xCl_2 \cdot 2H_2O$ system exhibits behavior close to that predicted by Fishman and Aharony[5(b)] for the model Hamiltonian system. We do not have an unambiguous explanation for the difference between our system and the others. One obvious difference is that $Fe_{1-x}Co_xCl_2 \cdot 2H_2O$ is an Ising-Ising mixture, whereas the others are, to leading order, Ising-XY systems. However, as stressed by Aharony[16] this should make no important difference except in the immediate vicinity of the tetracritical point where the Ising-Ising system will be more effectively decoupled.

The most straightforward explanation is that the random-field effects are much weaker in our system. By comparison with $Fe_xCo_{1-x}Cl_2$, at least, there is an obvious origin for this difference. In $Fe_xCo_{1-x}Cl_2$ the Fe^{2+} moment has an effective spin $S=1$ with comparable spin and orbital contributions to the moment.[17] In low-symmetry configurations this makes allowed off-diagonal couplings such as $J_{xz}S_xS_z$ which may be as large as the more usual diagonal terms. As first discussed by Wong *et al.*,[7] such off-diagonal couplings produce a site random field below T_H. In $Fe_{1-x}Co_xCl_2 \cdot 2H_2O$ the Fe^{2+} orbital moment is quenched[18] so that the Fe^{2+} moment is nearly pure spin $S=2$. This, in turn, should cause the off-diagonal interaction to be much weaker than the diagonal terms. Nakanishi's magnetostrictive mechanism[12] is also much weaker for orbital singlets.

More detailed studies of the tetracritical behavior in $Fe_{1-x}Co_xCl_2 \cdot 2H_2O$ would be quite valuable. Specifically, studies of the critical behavior in the tetracritical region should be possible, provided that concentration-gradient effects are minimized. These would make possible a more detailed test of the applicability of the Fishman-Aharony theory to this model Ising-Ising competing anisotropy random mixture.

ACKNOWLEDGMENTS

We would like to thank A. Aharony, R. A. Cowley, P. M. Horn, K. Nakanishi, M. Oku, and P. Wong for helpful discussions. This work was carried out as part of the U.S.—Japan Cooperative Neutron Scattering Program. The work done in Japan was partially supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture and by the Yamada Science Foundation. Work at Brookhaven National Laboratory was supported by the Division of Materials Sciences, U.S. Department of Energy, under Contract No. DE-AC02-76CH00016. Research at Massachusetts Institute of Technology was supported by the National Science Foundation—Low Temperature Physics Program under Grant No. DMR-79-23203.

*Permanent address: Institute for Solid State Physics, University of Tokyo, Roppongi, Minatoku, Tokyo 106, Japan.

[1]K. Katsumata, J. Magn. Magn. Mater. **31-34**, 1435 (1983).

[2]R. J. Birgeneau, R. A. Cowley, G. Shirane, and H. Yoshizawa, J. Stat. Phys. **34**, 817 (1984), and references therein.

[3]Y. Imry, J. Stat. Phys. **34**, 849 (1984); A. Aharony, *ibid.* **34**, 931 (1984).

[4]F. Matsubara and S. Inawashiro, J. Phys. Soc. Jpn. **42**, 1529 (1977).

[5](a) A. Aharony and S. Fishman, Phys. Rev. Lett. **37**, 1587 (1976); (b) S. Fishman and A. Aharony, Phys. Rev. B **18**, 3507 (1978).

[6]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).

[7]Po-zen Wong, P. M. Horn, R. J. Birgeneau, C. R. Safinya, and G. Shirane, Phys. Rev. Lett. **45**, 1974 (1980); P. Wong, P. M. Horn, R. J. Birgeneau, and G. Shirane, Phys. Rev. B **27**, 428 (1983).

[8]A. Ito, S. Morimoto, Y. Someya, H. Ikeda, Y. Syono, and H. Takei, Solid State Commun. **41**, 507 (1982); A. Ito, S. Morimoto, Y. Someya, Y. Syono, and H. Takei, J. Phys. Soc. Jpn. **51**, 3173 (1982).

[9]A. Ito, Y. Someya, and K. Katsumata, Solid State Commun. **36**, 681 (1980).

[10]D. Mukamel, Phys. Rev. Lett. **46**, 845 (1981).

[11]W. A. H. M. Vlak, E. Frikee, A. F. M. Arts, and H. W. de Wijn, J. Phys. C **16**, L1015 (1983).

[12]N. Nakanishi (unpublished).

[13]D. E. Cox, G. Shirane, B. C. Frazer, and A. Narath, J. Appl. Phys. **37**, 1126 (1966).

[14]A. Narath, Phys. Rev. **139**, A1221 (1965).

[15]W. Schneider and H. Weitzel, Solid State Commun. **13**, 303 (1973).

[16]A. Aharony (private communication).

[17]R. J. Birgeneau, W. B. Yelon, E. Cohen, and J. Makovsky, Phys. Rev. B **5**, 2607 (1972).

[18]K. A. Hay and J. B. Torrance, Jr., Phys. Rev. B **2**, 746 (1970).