Ferromagnetic resonance of the two-dimensional randomly mixed and diluted systems

$K_2Cu_{1-x}M_xF_4$ (M identical to Co, Mn, Zn) with very low concentration of M

Ferromagnetic resonance of the two-dimensional randomly mixed and diluted systems $K_2Cu_{1-x}M_xF_4$ (M ≡ Co, Mn, Zn) with very low concentration of M

T Anbe†, Y Yamaguchi†, M Itoh†, I Yamada†‡, H Fujii§ and M Hidaka§

† Department of Physics, Faculty of Science, Chiba University, Yayoi-cho, Chiba-260, Japan
§ Department of Physics, Faculty of Science, Kyushu University, Hakozaki, Fukuoka-812, Japan

Abstract. We report the experimental results of ferromagnetic resonance (FMR) of the two-dimensional randomly mixed systems $K_2Cu_{1-x}Co_xF_4$ and $K_2Cu_{1-x}Mn_xF_4$ with very low concentration of Co^{2+} and Mn^{2+}, respectively. Both the resonance field and the linewidth show strong angular variations in the c plane having fourfold symmetries; the easy axes are parallel to the [110] directions in the unit cell of K_2NiF_4-type structure and the linewidth is greatest along the hard axes, i.e. the [100] directions. These anisotropic behaviours are enhanced when the concentration of Co^{2+} (Mn^{2+}) is increased. It is worth noting an early report by Yamazaki *et al* that the FMR line of K_2CuF_4 has a very small fourfold anisotropic behaviour in the c plane; the easy axes are parallel to the [100] directions and the linewdith is greatest along the easy axes, contrary to the present results of the mixed systems. The angular behaviour of the FMR line observed in the diluted system $K_2Cu_{1-x}Zn_xF_4$ are substantially similar to that of K_2CuF_4.

1. Introduction

The compound K_2CuF_4 is a well known 2d Heisenberg ferromagnet. Below $T_c = 6.25$ K, spins lie in the c plane owing to a small XY-like anisotropy coming from both the anisotropic exchange and the dipolar interactions (Yamada 1972). Concerning the out-of-plane anisotropy, several studies of magnetic resonance have been reported (Yamazaki 1974, Borovik-Romanov *et al* 1980, Griev *et al* 1984). In the c plane, however, there is no reason to fix the direction of spins because of $S = \frac{1}{2}$ on the square lattice. Actually, it has been reported that the NMR signal of a single crystal of this compound observed under zero field shows a two-dimensional powder pattern indicating the absence of any easy axes of spins in the c plane (Kubo 1978). On the other hand, the experiments of ferromagnetic resonance (FMR) made under an external field of 2–3 kOe revealed a very weak fourfold anisotropy in the c plane (Yamazaki *et al* 1981, hereafter referred to as I). That is, both the linewidth and the resonance field show fourfold anisotropic behaviours below T_c; from the angular dependence of the resonance field in the c plane, the easy axes are found to lie parallel to the [100] directions in the unit cell

‡ Author to whom all correspondence should be addressed.

of K_2NiF_4-type structure and the anisotropy field extrapolated to $T = 0$ K is 5 Oe. Further, the linewidth is widest along the easy directions of magnetisation.

Based on the fact introduced above, we are interested in a spin arrangement when a small number of Cu^{2+} ions are displaced by other kinds of iron-group ions. Let us take the cases of Co^{2+} and Mn^{2+}, namely $K_2Cu_{1-x}Co_xF_4$ (abbreviated to Cu–Co) and $K_2Cu_{1-x}Mn_xF_4$ (Cu–Mn). When x is very small, most of the Co^{2+} (Mn^{2+}) are isolated from each other. Then, each CoF_6 (MnF_6) octahedron should be distorted because CuF_6 surrounding CoF_6 (MnF_6) are distorted due to the cooperative Jahn–Teller effect. In such a case, a difference should arise between the effect of Co^{2+} and Mn^{2+} on a net spin arrangement in the c plane because the spin of Co^{2+} is strongly connected with its F^--ligand field whereas the spin of Mn^{2+} has almost no connection with its F^--ligand because of its $L = 0$ state. When we see the whole range of x ($0 < x < 1$), Cu–Co (Cu–Mn) is recognised as a mixed system of K_2CuF_4 and the 2d Ising antiferromagnet K_2CoF_4 (2d Heisenberg antiferromagnet K_2MnF_4). It has been confirmed by the measurements of susceptibility that both systems show three magnetic phases with increasing x because of the competition between the ferromagnetic and the antiferromagnetic exchange interactions, namely ferromagnetic, spin-glass-like and antiferromagnetic phases; Cu–Co and Cu–Mn are ferromagnetic for $x < 0.2$ (Itoh *et al* 1989a) and $x < 0.2$ (Kimishima *et al* 1986), respectively. A purpose of the present study is to investigate a ground state of spins in these mixed systems with very small x by FMR experiments. Besides on these samples, we also made experiments on the sample of $x = 0$, i.e. K_2CuF_4 to reconfirm the anisotropic behaviour of the FMR line reported in I. Furthermore, we investigated the FMR of a sample of $K_2Cu_{1-x}Zn_xF_4$ (Cu–Zn) having $x = 0.05$ ($T_c = 5.4$ K estimated from the phase diagram determined by Okuda *et al* (1980)) to compare its result with those of Cu–Co and Cu–Mn. From our experiments, it has been found that both Cu–Co and Cu–Mn having very small x show similar fourfold in-plane anisotropic behaviour of the resonance field and also of the linewidth; the easy axes of the bulk magnetisation (or macroscopic magnetisation) are parallel to the [110] directions, contrary to the cases of K_2CuF_4 and Cu–Zn and the linewidth is widest along the hard axes, i.e. the [100] directions, which is also different from that of K_2CuF_4 and Cu–Zn.

2. Experimental procedure

To grow single crystals of the mixed systems, we first prepared $KCuF_3$, $KMnF_3$ and $KCoF_3$ from aqueous solutions. Then, a mixture of $KCuF_3$, $KMnF_3$ ($KCoF_3$) and KF was melted at about 900 °C in a platinum crucible and was cooled down to 700 °C over a period of 100 h. The method we used to grow Cu–Zn is reported elsewhere (Yamada *et al* 1983). The crystals thus obtained were analysed by an atomic absorption method to determine the composition x. For the present experiments, we used several samples having different compositions x less than 0.1, namely 0.003, 0.007, 0.01 and 0.08 for Cu–Co and 0.02, 0.04 and 0.07 for Cu–Mn. Since the proportion of Co(Mn) in each sample is very small, the T_c of the respective samples estimated from the phase diagrams of T_c against x (Itoh *et al* (1989a) for Cu–Co and Kimishima *et al* (1986) for Cu–Mn) is not that far from T_c K_2CuF_4 (6.25 K). In the samples of Cu–Co with $x = 0.001$–0.01, more than 96% of Co^{2+} ions are isolated from each other; thus we can interpret the experimental results without taking account of the competition of the exchange interactions. The FMR line of Cu–Co with $x = 0.08$ appeared to be completely different from those of

the samples with $x < 0.01$ and then we restrict our present report on Cu–Co for the samples with $x < 0.01$.

For $x = 0.07$ in Cu–Mn, the probability of isolation is 75% and thus we cannot say that most of Mn^{2+} are isolated from each other. However, the experimental data shown later can be explained qualitatively without taking account of the competition due to the exchange interactions. We include, therefore, the data for $x = 0.07$ in the present study. Each sample used was polished to form a sphere of diameter about 1 mm or less. Surface unevenness was approximately 20–50 μm. With these sphere samples and very weak microwave power referred to below, the magnetostatic mode (the Walker mode) did not appear.

FMR experiments were done by a conventional x-band spectrometer with a cylindrical cavity of TE_{111} mode. Since the absorption was very strong, the microwave power was reduced down to 10^{-3} μW to avoid saturation phenomena. The sample was placed on a top of a quartz rod of 3 mm diameter with its c axis roughly parallel to the axis of the rod; the rod was inserted horizontally into the cavity through a hole at one side. By a combination of rotating the rod around the horizontal axis and that of the external magnetic field H in the horizontal plane, we could obtain the condition of H being in the c plane and also in the ac plane exactly. After the FMR experiments, the [110] and [001] directions of each sample were identified by x-ray diffraction without removing the sample from the quartz rod.

3. Experimental results

Owing to the good sphericity of each sample and extremely low microwave power employed, the observed FMR lineshape was Lorentzian. The experiment was done over the temperature range 1.2–25 K including the paramagnetic region. The T_c of each sample is not that far from the T_c of K_2CuF_4 (6.25 K). Thus, the minimum temperature of the present work (1.2 K) is low enough to see the magnetic-ordering state of each sample.

At first, we re-examined the result for K_2CuF_4 reported in I. Our experiments at $T = 1.2$ K have reconfirmed the result in I. That is, H_{res} and ΔH_{pp} have different fourfold symmetries, namely H_{res} is lowest for $H \parallel$ [100] directions indicating that the [100] directions are easy axes, whereas ΔH_{pp} as a function of the angle φ between the [100] direction and H in the c plane behaves oppositely to H_{res}, being largest for $H \parallel$ [100]. Further, the angular variations of H_{res} and ΔH_{pp} in Cu–Zn with $x = 0.05$ observed at $T = 1.2$ K are similar to those of K_2CuF_4 as shown in figures 1(a) and 1(b), namely the broadest linewidth is observed along the axes of easy magnetisation in the c plane, i.e. the [100] directions. The in-plane anisotropy fields estimated from our data are approximately 4–6 Oe for both K_2CuF_4 and Cu–Zn with $x = 0.05$. On the other hand, the difference of ΔH_{pp} between $H \parallel$ [100] and $H \parallel$ [110] at $T = 1.2$ K is about 7 Oe for both. Thus, the substitution of small number of Cu^{2+} ions by non-magnetic ions Zn^{2+} brings about no substantial effect on the anisotropic behaviour of the FMR line observed in K_2CuF_4. We note here that the behaviours of H_{res} and ΔH_{pp} in both K_2CuF_4 and Cu–Zn as a function of φ are out-of-phase with each other.

Now, we show the results for Cu–Co. The φ dependence of H_{res} and ΔH_{pp} measured at 1.2 K are shown in figures 2(a) and 2(b), respectively; the respective change of H_{res} and ΔH_{pp} with φ shows a fourfold symmetry and the appearance of the minimum of H_{res} for $H \parallel$ [110] directions means that the easy magnetisation axes are along these directions.
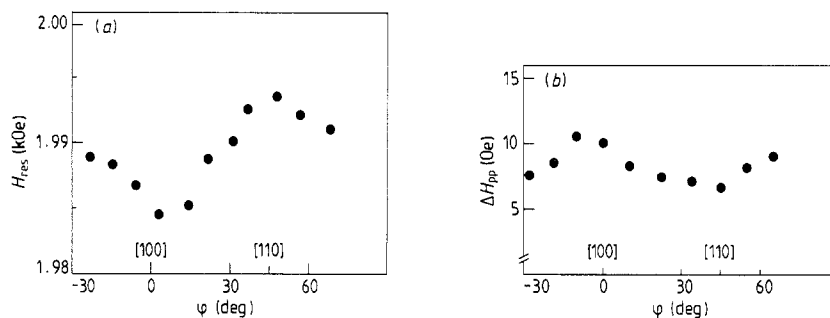
Figure 1. $K_2Cu_{1-x}Zn_xF_4$: in-plane angular dependence observed at $T = 1.2$ K of (a) the resonance field H_{res} at $\omega = 9.182$ GHz, and (b) the derivative peak-to-peak linewidth ΔH_{pp} for $x = 0.05$.

Figure 2. $K_2Cu_{1-x}Co_xF_4$: in-plane angular dependence observed at $T = 1.2$ K of (a) the resonance field H_{res} at $\omega = 9.184$ GHz an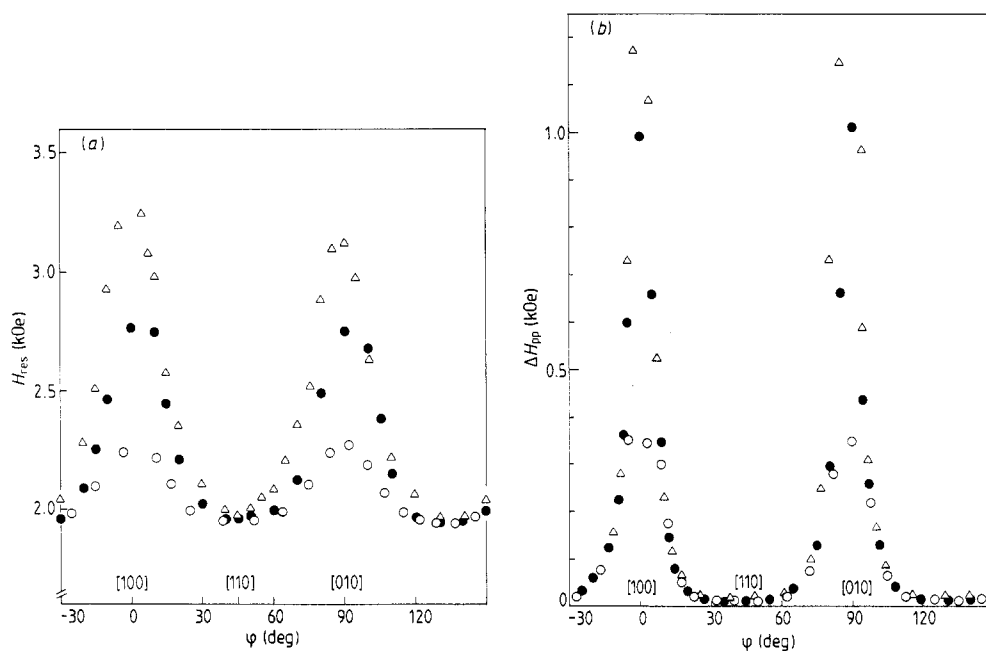d (b) the derivative peak-to-peak linewidth ΔH_{pp}. Both parts: $\bigcirc$, $x = 0.003$; $\bullet$, $x = 0.007$; $\triangle$, $x = 0.01$.

However, H_{res} versus φ and ΔH_{pp} versus φ are in-phase, namely both H_{res} and ΔH_{pp} show the minimum at the same angle, which is completely different from that of both K_2CuF_4 and Cu–Zn with $x = 0.05$. The anisotropic behaviours of H_{res} and ΔH_{pp} are enhanced remarkably when x is increased. The dependence of H_{res} on T is shown in figure 3 for $x = 0.007$; H_{res} for $\boldsymbol{H} \parallel [110]$ and $\boldsymbol{H} \parallel [100]$, together with that for $\boldsymbol{H} \parallel [001]$, i.e. $\boldsymbol{H} \parallel \boldsymbol{c}$ are shown. Similar changes were observed in the samples of $x = 0.003$ and $x = 0.01$. We can see in this figure that the anisotropic behaviour of H_{res} in the c plane becomes weaker with the increasing T and disappears approximately above 10 K; above this temperature, the system goes into the para-magnetic region. The difference between
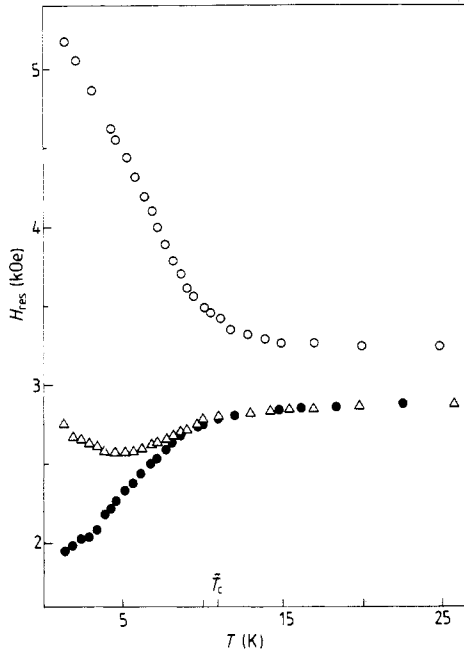
Figure 3. $K_2Cu_{1-x}Co_xF_4$: temperature dependence of the resonance field H_{res} at $\omega = 9.184$ GHz for $x = 0.007$. $\bigcirc$, $\boldsymbol{H} \parallel [001]$; $\triangle$, $\boldsymbol{H} \parallel [100]$; $\bullet$, $\boldsymbol{H} \parallel [110]$.
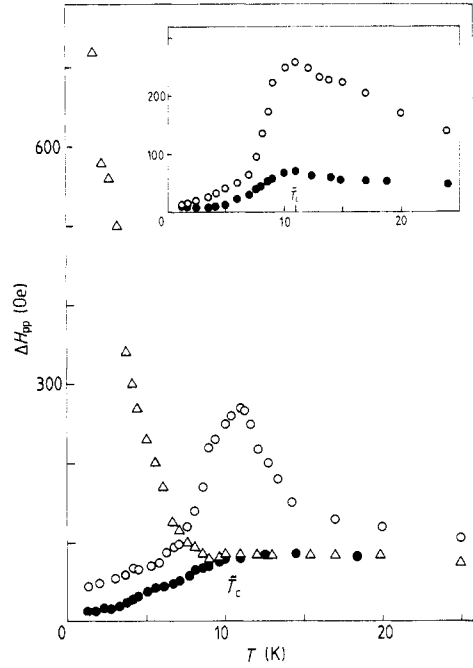
Figure 4. $K_2Cu_{1-x}Co_xF_4$: temperature dependence of the derivative peak-to-peak linewidth ΔH_{pp} for $x = 0.007$. Inset: the same for K_2CuF_4. (The anisotropy of ΔH_{pp} in the c plane is less than 5 Oe.) The symbols are as defined in figure 3.

H_{res} for $\boldsymbol{H} \parallel c$ and $\boldsymbol{H} \perp c$ in the para-magnetic region arises from the different values of g_a and g_c, where g_a and g_c are the g-values determined for $\boldsymbol{H} \perp c$, and $\boldsymbol{H} \parallel c$ respectively; we found that both g_a and g_c of all the samples used in the present experiment were not very different from those of K_2CuF_4, namely $g_a = 2.29$ and $g_c = 2.09$.

On the other hand, the temperature dependence of ΔH_{pp} for $x = 0.007$ is shown in figure 4 for $\boldsymbol{H} \parallel [110]$, [100] and [001]; A peak of ΔH_{pp} for $\boldsymbol{H} \parallel [001]$ around $T = 10$ K means that spin ordering develops below this T in a field H of about 3 kOe. From now on, the temperature at which a peak of ΔH_{pp} for $\boldsymbol{H} \parallel [001]$ appears is denoted as $\tilde{T}_c$ after Yamada *et al* (1983). $\tilde{T}_c$ does not coincide with T_c because the external field of 2–3 kOe couples directly with the magnetisation and then the true ferromagnetic phase transition is wiped out. In the present cases, the ferromagnetic phenomena appears below $\tilde{T}_c$. $\tilde{T}_c$ rather corresponds to the position of the broad peak appearing in the magnetic specific heat, indicating a development of the two-dimensional short-range order (Yamada 1972) and is then not so sensitive to x as that of T_c for very small x. To make a comparison with pure K_2CuF_4, ΔH_{pp} around $\tilde{T}_c$ for K_2CuF_4 is shown in the inset of figure 4.

The results for Cu–Mn are similar to those of Cu–Co as shown in figures 5(a) and 5(b). That is, the changes of H_{res} and ΔH_{pp} with φ are in-phase. From the φ-dependence of H_{res}, we find that the easy magnetisation axes are parallel to the [110] directions. The amplitudes of the angular variation of both ΔH_{pp} and H_{res} are very small compared with those of Cu–Co. The dependence of H_{res} and ΔH_{pp} on T is shown in figure 6. The anisotropic behaviour in the c plane also disappears around $\tilde{T}_c$, in a similar way to the Cu–Co case.
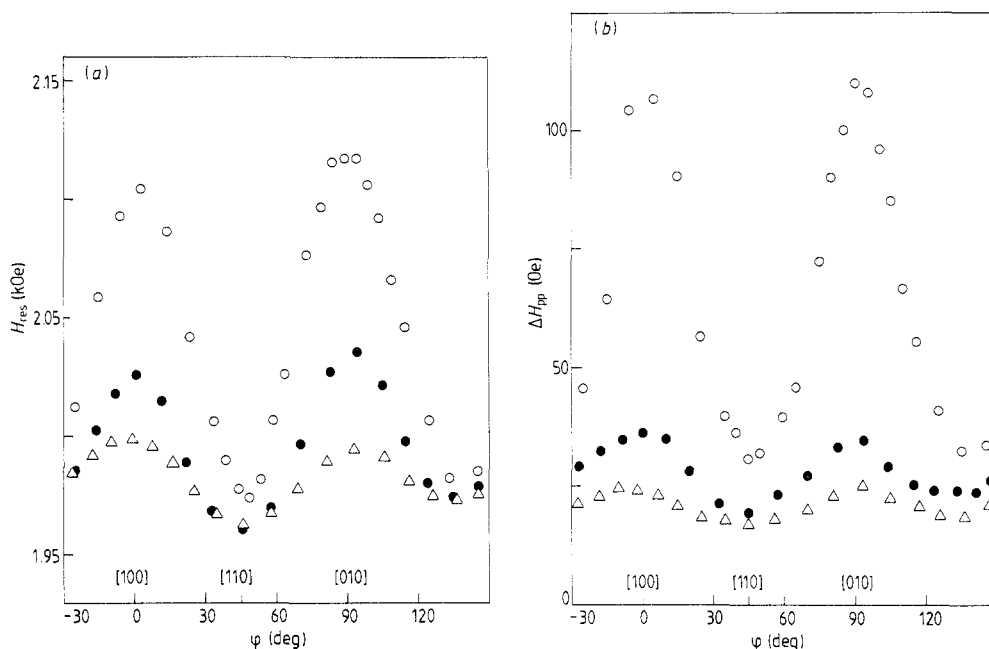
Figure 5. $K_2Cu_{1-x}Mn_xF_4$: in-plane angular dependence observed at $T = 1.2$ K of (a) the resonance field H_{res} at $\omega = 9.191$ GHz and (b) the derivative peak-to-peak linewidth ΔH_{pp}. Both parts: $\triangle$, $x = 0.02$; $\bullet$, $x = 0.04$; $\bigcirc$, $x = 0.07$.

4. Discussion

Let us discuss the results for the mixed systems, leaving those of K_2CuF_4 and Cu–Zn until later. Since the angular variations of both H_{res} and ΔH_{pp} in K_2CuF_4 are very small compared with those of the mixed systems, we neglect them in the discussion for the mixed systems. In addition to the out-of-plane anisotropy field H_{A1}, we postulate an in-plain effective anisotropy field H_{A3} to explain the H_{res} versus φ variation. Following a conventional theory of FMR for a system having tetragonal anisotropy energy, we obtain an equation of a frequency–field relation by solving a torque equation as:

$$(\omega/\gamma)^2 = (H_{res} - H_{A3}\cos4\varphi)[H_{res} + H_{A1} - \tfrac{1}{4}H_{A3}(\cos4\varphi + 3)] \qquad (1)$$

where ω is a resonance frequency. To derive equation (1), the effects of the demagnetisation field do not need to be considered because the samples are spherical. When spins lie in the c plane, it appears that $H_{A1} > 0$. On the other hand, we find that $H_{A3} < 0$ for K_2CuF_4 and Cu–Zn, whereas $H_{A3} > 0$ for Cu–Co and Cu–Mn reflecting the difference of the direction of easy magnetisation. Introducing the experimental values of $H_{res}(T \to 0$ K) for $\varphi = 0$ and $\pi/4$ into equation (3), we obtain H_{A3}. The dependence of both H_{A1} and H_{A3} on x is shown in figure 7(a) for Cu–Co and figure 7(b) for Cu–Mn; H_{A3} increases almost linearly with x and H_{A1} decreases with increasing x.

An origin of the variation of H_{A3} can be explained qualitatively as follows. So long as x is very small, each CoF_6 (MnF_6) is isolated from any other and is obliged to be distorted because the surrounding CuF_6 are distorted cooperatively. A spin of Co^{2+} in a ligand field with low symmetry should be aligned along one of the principal axes of the ligand field because of the strong effect of the ligand field on the Co^{2+}-spin. Now, let us
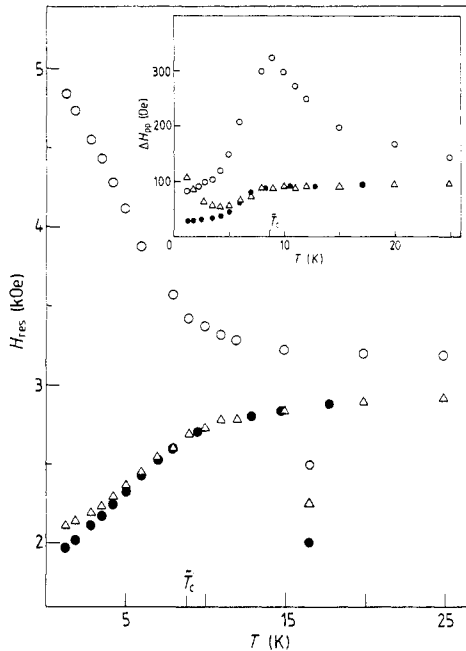
Figure 6. $K_2Cu_{1-x}Mn_xF_4$: temperature dependence of the resonance field H_{res} at $\omega = 9.191$ GHz for $x = 0.07$. Inset: the derivative peak-to-peak linewidth ΔH_{pp} for $x = 0.07$. The symbols are as defined in figure 3.
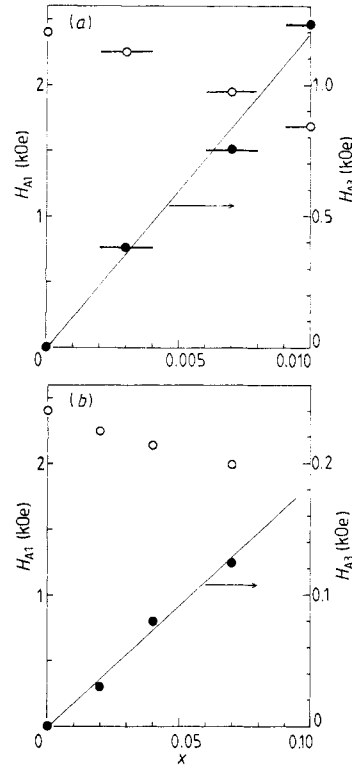
Figure 7. ●, in-plane effective anisotropy field H_{A3} and ○, out-of-plane anisotropy field H_{A}; versus concentration x: (a) M ≡ Co^{2+}, and (b) M ≡ Mn^{2+}, in $K_2Cu_{1-x}M_xF_4$.

suppose that a spin of Co^{2+} has a direction parallel to the longest axis of the distorted CoF_6. Since the distorted F^- octahedra are arranged with their longest axes orthogonal to each other in the c plane, then each spin of Co^{2+} has two choices for its direction, parallel to the [100] direction or parallel to the [010] direction. Since each Co^{2+} spin in the present mixed compound couples antiferromagnetically with its neighbouring Cu^{2+} spins (Ferré and Régis 1978, Itoh *et al* 1989b), the spins of Cu^{2+} located not far from each Co^{2+} are forced to align along the [100] or [010] directions depending on the direction of the respective Co^{2+} spin they surround. We call these two groups of Cu^{2+} spins [100] clusters and [010] clusters, respectively. Then, majority of Cu spins far from these two kinds of clusters are obliged to align along the [110] directions. This is why the net magnetisation has easy axes along the [110] directions.

From the argument developed above, we can attribute H_{A3} in Cu–Co with $x < 0.01$ solely to the anisotropic exchange between a Co^{2+} spin and nearest-neighbour Cu^{2+} spins, because the anisotropic exchange of Cu–Cu bonding is absent in the c plane and Co–Co bonding is neglected owing to $x \ll 1$. Considering that half of the number of Co^{2+} make [100] or [010] clusters, then we obtain the Hamiltonian expressing the anisotropy along the [100] axis as

$$\mathcal{H}_{anis} = -2\frac{P(Cu-Co)}{2} \sum [J_{\parallel}S_i^z s_j^z + J_{\perp}(S_i^x s_j^x + S_i^y s_j^y)] \tag{2}$$

where S_i and s_j are spins of Co^{2+} and Cu^{2+}, respectively and $P(Cu-Co)$ is a probability

of Cu–Co bonding; it is given as $P(\text{Cu–Co}) = 2x(1 - x) \simeq 2x$ for small x. In equation (2), the z axis is along the [100] axis. Using the molecular field approximation, the anisotropy field $H_{\text{A}}^{[100]}$ along the [100] axis is given as

$$H_{\text{A}}^{[100]} = 2z(J_{\parallel} - J_{-})sx/g\mu_{\text{B}} \qquad (3)$$

where z is the number of Cu^{2+} which couple with Co^{2+}. Co^{2+} ions in [010] clusters also produce the anisotropy field $H_{\text{A}}^{[010]}$ along the [010] axis which is given by the same expression as equation (3). Then, the observed $H_{\text{A}3}$ should be given by $H_{\text{A}3} = \sqrt{2}H_{\text{A}}^{[100]}$. We put $z = 2$ following a proposal by Ferré an Régis (1978), that is, a magnetic ions introduced in K_2CuF_4 has exchange couplings with only two Cu^{2+} among four nearest-neighbour Cu^{2+} because of the orthogonal orbital ordering of $d(x^2 - z^2)$ and $d(y^2 - z^2)$. Using the value of $g = 6.3(\text{Co}^{2+})$, $s = \frac{1}{2}$ and the data for $H_{\text{A}3}$ versus x given in figure 7(a), we obtain $|J_{\parallel} - J_{\perp}| = 18$ K. This value is smaller than that of K_2CoF_4, $J_{\parallel} = -97$ K and $J_{\perp} = -29$ K (Breed *et al* 1969), $J_{\parallel} = -95.1$ K and $J_{-} = -43.3$ K (Goto *et al* 1989) or that of Rb_2CoF_4, $J_{\parallel} = -89.7$ K and $J_{\perp} = -49.6$ K (Ikeda and Hutchings 1978). Considering the coupling of Co^{2+} with Heisenberg-type ions Cu^{2+}, we understand the smaller value of the exchange anisotropy determined above. On the other hand, before the experiments on Cu–Mn we thought that a fourfold anisotropy as observed in Cu–Co with $x < 0.01$ could not be expected because Mn^{2+} has no connection with the ligand field owing to its $L = 0$ state. The unexpected result shown in § 3 can be understood as follows: when the fourth-order perturbation is considered, a Mn^{2+} ion comes to have a small anisotropy like a single-ion type $D(S^z)^2$. Then, the spin of Mn^{2+} is also put in a situation similar to that of Co^{2+}, although the force to fix the Mn^{2+} spin to one of the principal axes of the ligand field is very weak compared with that of the Cu–Co case. Mn^{2+} in the [100] and [010] clusters produce orthogonal anisotropy fields each having the value of $(DS/2g\mu_{\text{B}})x$. Then, $H_{\text{A}3}$ can be given as

$$H_{\text{A}3} = (DS/\sqrt{2}g\mu_{\text{B}})x.$$

Using $S = \frac{5}{2}$, $g = 2.0$ and our data for $H_{\text{A}3}$ versus x shown in figure 7(b), we obtain $D = 0.14$ K (1.0 kOe).

Let us compare this value of D with that of Mn^{2+} determined in other compounds, for example, $D = 5 \times 10^{-3}$ K (39 Oe) in K_2ZnF_4 : Mn^{2+} (Folen 1972) and $D = 0.04$ K (326 Oe) in CsMgCl_3 : Mn^{2+} (McPherson *et al* 1970). Since the ligand field in K_2ZnF_4 is highly symmetric, D is very small. On the other hand, a Cl-octahedron around a Mn^{2+} in CsMgCl_3 is distorted and then D is larger than for K_2ZnF_4 : Mn^{2+}. In the present case, a fairly large distortion of MnF_6 is expected because of the cooperative Jahn–Teller distortion of the surrounding CuF_6. Thus $D = 0.14$ K is reasonable. Owing to the single-ion-type anisotropy of Mn^{2+}, Cu–Mn with $x \leqslant 0.07$ should have a spin arrangement similar to that of Cu–Co, although the direction of each Mn^{2+} spin should deviate from the principal axes of the ligand field because of the weak connection of the Mn^{2+} spins with the ligand field.

The observed $H_{\text{A}1}$ decreases gradually with x; at some x, then, $H_{\text{A}1}$ will become zero and the net moment cannot be in the c plane below that x. With the increasing x, however, the probability of Co–Co (Mn–Mn) bonding increases and then the situation becomes complicated.

As for ΔH_{pp} versus φ, we give only a qualitative argument. The fourfold change of ΔH_{pp} observed in the mixed systems is understood when we consider the spatial fluctuations $\delta H_{\text{A}3}$ of $H_{\text{A}3}$ arising from the inhomogeneous distribution of Co^{2+} spins (Mn^{2+} spins) having preferred directions of [100] or [010]. When $\boldsymbol{H}$ is parallel to one of

the hard axes in the c plane, i.e. $\boldsymbol{H} \parallel [100]$ (or $[010]$), $[(\delta H_{A3}^2)_{av}]^{1/2}$ along the $[010]$ (or $[100]$) direction should disturb the uniform precession of the total magnetic moment and then ΔH_{pp} along these hard axes becomes wide. Further, ΔH_{pp} for these directions increases with decreasing temperature owing to the increase of the root-mean-square of δH_{A3}. For $\boldsymbol{H} \parallel [001]$, the resonance does not reflect the inhomogeneity of H_{A3}. Thus, ΔH_{pp} along the $[001]$ direction is not so wide as compared with that of K_2CuF_4.

ΔH_{pp} versus T in K_2CuF_4 near $\tilde{T}_c$ has been discussed in detail in an early paper by Yamada et al (1983). In short, the anomalous increase of $\Delta H_{pp}(\boldsymbol{H} \parallel [001])$ with T approaching $\tilde{T}_c$ from above indicates a growth of the spin fluctuation, namely the development of the long-wavelength mode ($q \sim 0$) of the spin-fluctuation enhances the secular part of the perturbation term (the dipole–dipole and the anisotropic exchange interaction) and then ΔH_{pp} shows the angular behaviour of $(3\cos^2\theta - 1)^2$ in the ac plane where θ is the angle between $\boldsymbol{H}$ and $[001]$. The ratio $\Delta H_{pp}(\boldsymbol{H} \parallel c)/\Delta H_{pp}(\boldsymbol{H} \perp c) \simeq 3.8$ at $\tilde{T}_c$ obtained experimentally realises the expected value 4. For Cu–Co with $x < 0.01$, this ratio is about 3.3–3.8, which means that the uniform long-wavelength mode of the spin fluctuation is still maintained. As referred to in § 1, Cu–Co with $x = 0.08$ showed a value far below 4 indicating some other spin ordering.

Based on the above discussion, we again look at the results for K_2CuF_4 and Cu–Zn. Before we got the results for the mixed systems, we could not rule out the possibility of the effect of unexpected magnetic impurities in K_2CuF_4 being a source of the in-plane anisotropy. However, the results for the mixed systems allay this fear because the anisotropy caused by the magnetic impurities (i.e. Co^{2+} or Mn^{2+}) is completely different from that observed in K_2CuF_4 or in Cu–Zn. Considering that the FMR measurements were done under an external field of 2–3 kOe, one possible origin of the in-plane anisotropy is a field-induced magnetostriction (Hirakawa and Yamazaki 1988). We believe that this forced magnetostriction under the external field of 2–3 kOe is not very strong and its effect is easily overwhelmed by that of the magnetic impurities. Further studies are necessary to clarify the origin of the in-plane anisotropy in K_2CuF_4.

In conclusion, a small number of Co^{2+} (Mn^{2+}) ions introduced into K_2CuF_4 bring about a strong effect on the FMR line. Both the resonance field and the linewidth show fourfold symmetry in the c plane; the linewidth is narrowest for the direction of the easy magnetisation axes $[110]$, which is completely different from that of K_2CuF_4 and the diluted system $K_2Cu_{1-x}Zn_xF_4$. The anisotropy in the c plane observed in the mixed systems is explained as being due to the distortion of a CoF_6 (MnF_6) octahedron surrounded by CuF_6. From the present work, we have clarified that the cooperative Jahn–Teller distortion of CuF_6 still plays an important role even in the mixed systems.

References

Borovik-Romanov A S, Kreines N M, Laiho R, Levola T and Zholikov V G 1980 $J.$ $Phys.$ $C:$ $Solid$ $State$ $Phys.$
    13 879
Breed D J, Gilijamse K and Miedema A R 1969 $Physica$ **45** 205

Ferré J and Régis M 1978 *Solid State Commun.* **26** 225

Folen V J 1972 *Phys. Rev.* B **6** 1670

Goto T, Nakao K, Sakakibara T, Itoh M and Yamada I 1989 *J. Phys. Soc. Japan* at press

Griev T, Kullmann W, Fehr P, Strobel K and Geik R 1984 *J. Phys. C: Solid State Phys.* **17** 6843

Hirakawa K and Yamazaki H 1988 private communication

Ikeda H and Hutchings M T 1978 *J. Phys. C: Solid State Phys.* **11** L529

Itoh M, Yamada I, Kobayashi T, Ishizuka M, Amaya K, Koga K and Motoya K 1989a *J. Phys. Soc. Japan* at press

Itoh M, Yamada I, Sakakibara T and Goto T 1989b *J. Phys. Soc. Japan* **58** 684

Kimishima Y, Ikeda H, Furukawa A and Nagano H 1986 *J. Phys. Soc. Japan* **55** 3574

Kubo H 1978 private communication

McPherson G L, Kistenmacher Y J and Stucky G D 1970 *J. Chem. Phys.* **52** 815

Okuda Y, Tohi Y, Yamada I and Haseda T 1980 *J. Phys. Soc. Japan* **49** 936

Yamada I 1972 *J. Phys. Soc. Japan* **33** 979

Yamada I, Morishita I and Tokuyama T 1983 *Physica* B **115** 179

Yamazaki H 1974 *J. Phys. Soc. Japan* **37** 667

Yamazaki H, Morishige Y and Chikamatsu M 1981 *J. Phys. Soc. Japan* **50** 2872