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Abstract. Magnetic excitations in $Rb_2Co_cNi_{1-c}F_4$ have been investigated. Neutron scattering experiments were performed on single crystals with $c = 0.14$ and 0.7. Two bands of excitations have been observed. Spin-wave dispersion relations obtained at 15 K are compared with calculated dispersion curves based on the mean-crystal model. Although the model gives a qualitative description of the concentration dependences of the dispersion relations, good agreement is not obtained when the exchange interaction parameters determined for pure crystals are used. The possibility of a change in the exchange interaction parameter between Co ions in the mixed crystal is discussed.

1. Introduction

The nature of the magnetic excitations in disordered systems has been extensively studied. Many kinds of insulating antiferromagnetic random alloy which have transition-metal fluorides as a base have been investigated both experimentally using neutron scattering and theoretically. In particular, materials which have the so-called K_2NiF_4-type crystal structure are considered to be ideal two-dimensional (2D) systems and the Hamiltonian can be described in a simple form with only nearest-neighbour exchange interaction within a 2D square lattice. Materials such as $Rb_2Mn_{0.5}Ni_{0.5}F_4$ (Birgeneau *et al* 1975), $Rb_2Mn_cMg_{1-c}F_4$ (Cowley *et al* 1977) and $Rb_2Co_{0.5}Ni_{0.5}F_4$ (Ikeda *et al* 1983) have been investigated.

In random magnetic systems with two different types of magnetic ion, two bands of excitations which have an intrinsic energy width have been observed. Each magnetic excitation conserves the character of the magnetic excitation from one of two different magnetic ions. In $Rb_2Mn_{0.5}Ni_{0.5}F_4$ it has been shown that the dispersion relations of excitations are well described by a mean-crystal model with the use of the exchange interaction parameters J_{Mn-Mn}, J_{Ni-Ni} of the pure materials and an empirical relation $J_{Mn-Ni} = (J_{Mn-Mn}J_{Ni-Ni})^{1/2}$ (Cowley and Buyers 1972) for the exchange interaction between Mn and Ni ions. It has also been demonstrated that the simple Ising cluster model is applicable to describe the zone boundary response. The computer simulations (Thorpe and Alben 1976) reproduce the experimental results very well for both energy and intensity distributions.
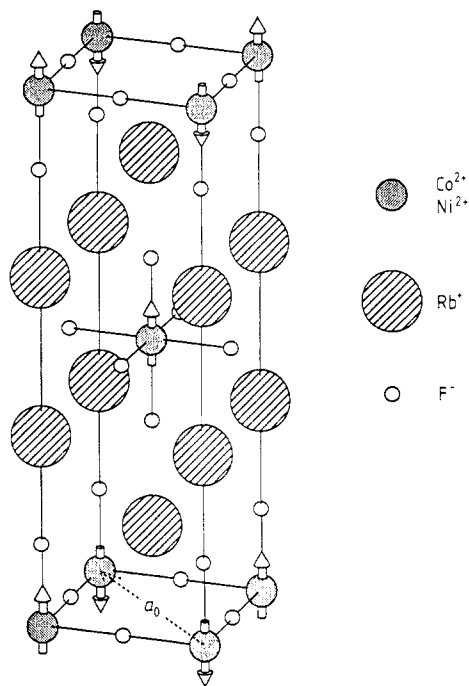
Figure 1. Crystal and magnetic structure of $Rb_2Co_cNi_{1-c}F_4$.

However, in $Rb_2Co_cNi_{1-c}F_4$ with a concentration c of 0.5† (Ikeda *et al* 1983) it has been found that the exchange interaction parameters in this mixed system should be significantly modified from those of the pure materials. The magnetic properties of crystals with $c = 0$ and $c = 1$ are quite different from each other. Rb_2CoF_4 exhibits 2D Ising behaviour while Rb_2NiF_4 shows a 2D Heisenberg-like character. In order to describe the magnetic excitation in this system, based on the mean-crystal model, Ikeda *et al* have deduced an expression for the dispersion relations of the system with an anisotropic exchange interaction and an arbitrary atomic concentration c. They have shown that the dispersion relations calculated by this model, as well as the zone boundary response calculated by the Ising cluster model, do not agree with the experimental results if the exchange parameters determined from the results of crystals with $c = 0$ and 1 and their geometrical mean for J_{Co-Ni} are used. It is important therefore to know the concentration dependences of the excitations in order to obtain a good description of the excitations in the $Rb_2Co_cNi_{1-c}F_4$ system. In the present study, measurements were carried out on $Rb_2Co_cNi_{1-c}F_4$ with two other concentrations $c = 0.14$ and 0.7. The crystal structure of $Rb_2Co_cNi_{1-c}F_4$ is shown in figure 1.

2. Experiments

The neutron inelastic scattering experiments have been carried out using the multi-analyser crystal spectrometer (MAX) installed at the spallation pulsed neutron source (KENS) of the National Laboratory for High Energy Physics (KEK), Tsukuba, Japan. The

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† The correct concentration of the sample reported in the reference as $c = 0.5$ has been proved to be 0.32 by a chemical analysis carried out recently.
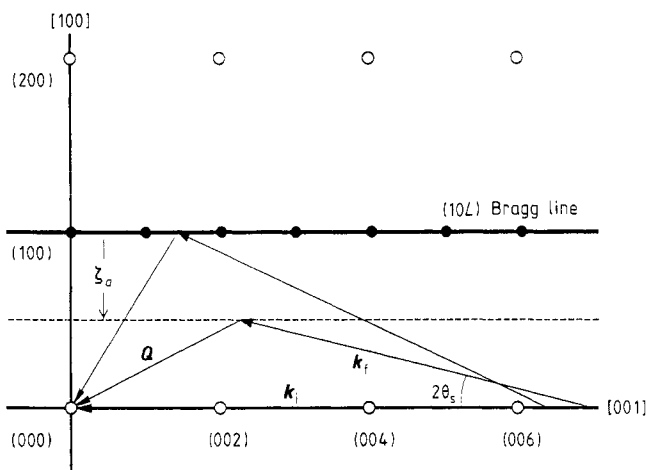
Figure 2. Scattering diagram showing the TOF scans made along the lines parallel to (10L) Bragg line.

important feature of MAX is that it enables us to observe collective excitations with a time-of-flight (TOF) method along a desired crystallographic direction. The details of MAX have been reported elsewhere (Tajima *et al* 1982, 1983).

The experiments were performed on single crystals of volume 1.4 cm^3 (for $c = 0.14$) and 1.2 cm^3 (for $c = 0.7$) grown by a Bridgman method. Special care was taken to grow homogeneously mixed crystals. The compositions were determined by a chemical analysis. The samples were cooled in a He refrigerator and the measurements were carried out at 15 K.

In the 2D magnets, it has been demonstrated that MAX can perform the constant-q measurements quite effectively for various q-values (Tajima *et al* 1988). The magnetic excitations depend only on the distance from the Bragg line and the TOF scans can be regarded as 'constant q' if the scan is made along a line parallel to the Bragg line. MAX is composed of 15 analyser–detector systems with different scattering angles. Therefore, when each of the detectors of MAX scans along the line approximately separated from the (10L) Bragg line, effective constant-q measurements with different q-values are available at the same time. For example, in this experiment the detector with lowest scattering angle ($2\theta_s = 10°$) made a scan along the line which was separated by 0.49 Å^{-1} from the (10L) Bragg line, and the TOF spectrum obtained with this detector is the constant-q spectrum with ζ_a ($= qa_0/2\pi$) $= 0.47$. Other data obtained at the same time with the detector at $2\theta_s = 14°$ correspond to $\zeta_a = 0.32$. In these scans, the magnitude of the scattering vector $Q = k_i - k_f$ varies throughout the TOF scan; therefore the observed intensity should be corrected by taking into account the change in the magnetic form factor $f(Q)$. A schematic representation of the scattering diagram is shown in figure 2. The analysers were pyrolytic graphite crystals. The energy resolution of the spectrometer was, for example, 4.5 meV (FWHM) for an energy transfer $\hbar\omega$ of 30 meV for the detector at the lowest scattering angle ($2\theta_s = 10°$) and was nearly the same magnitude for the other detectors.

3. Results and discussion

Examples of observed spectra are shown in figure 3 and the resultant dispersion relations are depicted in figure 4. In the figures the following features are apparent.
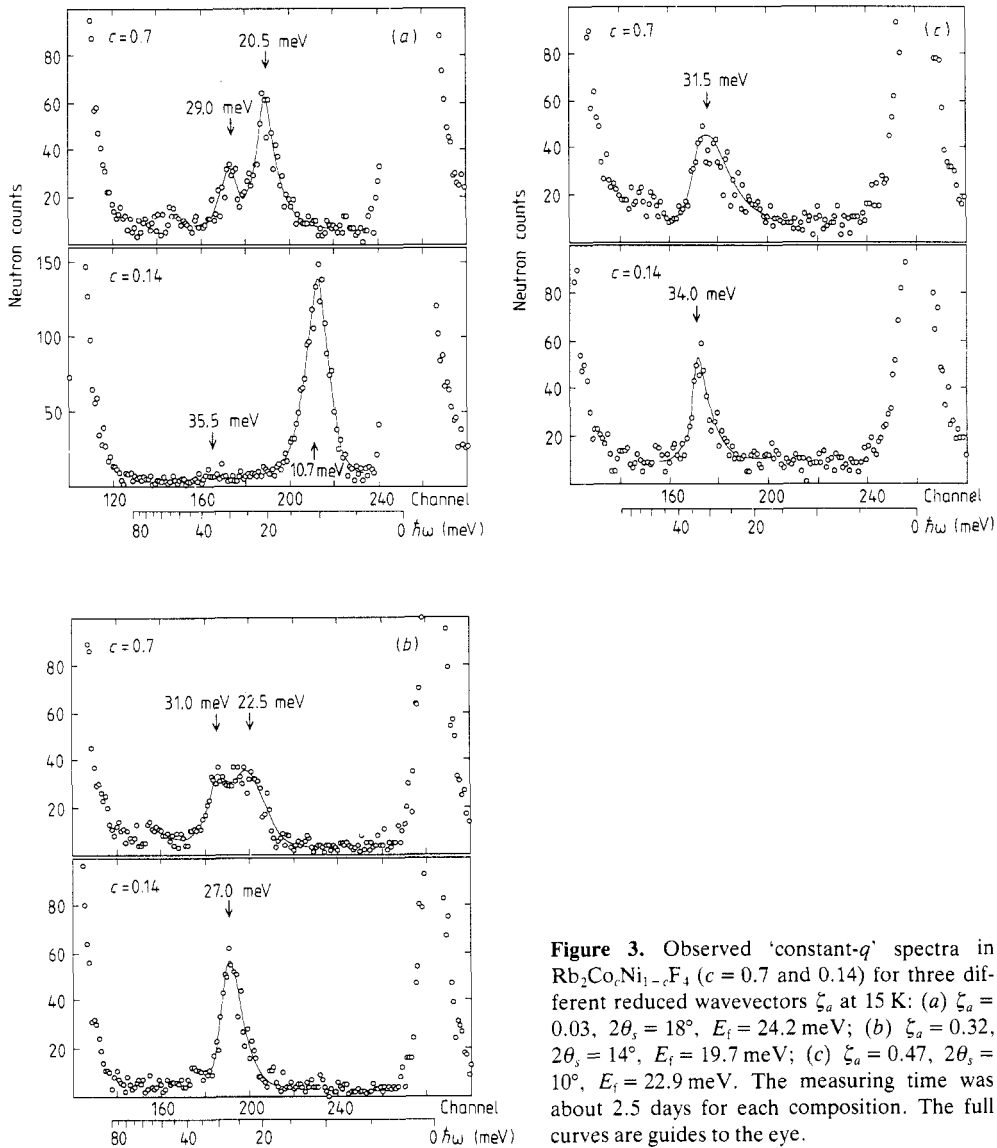
Figure 3. Observed 'constant-q' spectra in $Rb_2Co_cNi_{1-c}F_4$ ($c = 0.7$ and 0.14) for three different reduced wavevectors ζ_a at 15 K: (a) $\zeta_a = 0.03$, $2\theta_s = 18°$, $E_f = 24.2$ meV; (b) $\zeta_a = 0.32$, $2\theta_s = 14°$, $E_f = 19.7$ meV; (c) $\zeta_a = 0.47$, $2\theta_s = 10°$, $E_f = 22.9$ meV. The measuring time was about 2.5 days for each composition. The full curves are guides to the eye.

As expected, two excitation bands are observed. In a Ni-rich crystal ($c = 0.14$) the dispersion curve for the lower-energy mode resembles that of pure Ni. For $c = 0.7$, on the contrary, the dispersion relation for the higher-energy mode is similar to that of pure Co. As the concentration of Ni atoms is decreased, the lower-energy mode exhibits the character of localised excitations with less dispersion. A broad asymmetric peak, which can be seen in the upper part of figure 3(c), suggests the superposition of the two excitation bands.

Another peak, in addition to these two excitation bands, was observed at about $\hbar\omega = 55$ meV, and this excitation has no measurable dispersion. Since these peaks are more pronounced in the sample with higher Co^{2+} concentrations, this excitation may originate
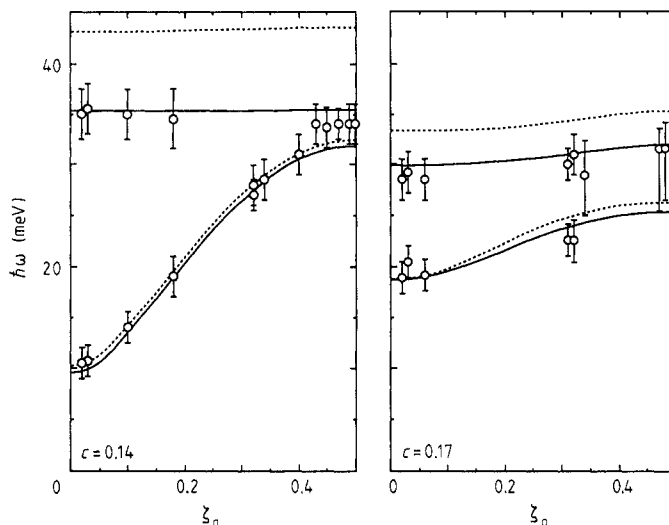
Figure 4. Dispersion relations for $Rb_2Co_cNi_{1-c}F_4$ ($c = 0.7$ and 0.14): - - -, curves calculated with the use of the exchange parameters for pure materials Rb_2CoF_4 and Rb_2NiF_4; ———, curves calculated with properly modified J_{Co-Co}.

Table 1. Lattice constants, Néel temperatures and exchange parameters in the pure crystals.

	a_0 (Å)	c_0 (Å)	T_N (K)	J (meV)	$g\mu_B H_A$ (meV)
Rb_2CoF_4	5.817	13.615	101	$J^{zz} = 7.73, J^{zz} = 4.25$	0.0
Rb_2NiF_4	5.733	13.550	98	$J^{zz} = J^{xx} = 4.2$	0.28

from the transition between the $j = \frac{1}{2}$ and $j = \frac{3}{2}$ manifold of Co^{2+} ions. No further investigations of this excitation were carried out.

The results were analysed using the expression for the dispersion relation given previously (Ikeda *et al* 1983). Applying Walker's four-sublattice model (Birgeneau *et al* 1975) and taking a configurational average over all possible local environments of a specific type of ion, we obtained two pairs of degenerate spin-wave modes by solving coupled equations. First, for all samples, exchange and anisotropy parameters which had been obtained for pure materials were used together with the geometric mean value for the exchange parameter between Co and Ni spins: $J_{Co-Ni} = (J_{Co-Co}J_{Ni-Ni})^{1/2}$. For Co^{2+} ions a fictitious spin $S' = \frac{1}{2}$ was assumed because experiments were performed at a sufficiently low temperature (15 K). The values of parameters are given in table 1 together with the lattice constants and Néel temperatures. As indicated by the broken curves in figure 4, this model describes the concentration dependences of the dispersion relations well, especially for the lower-energy modes which are associated with Ni^{2+} spin. For all samples, however, the excitation energies of upper modes associated with Co^{2+} spin are much lower than the calculated values.

It was also found that the discrepancy described above is removed, as indicated by the full curves in figure 4, if the parameter J_{Co-Co} is modified (reduced). As shown in figure 5, this reduction factor δ depends on c and the factor $1 - \delta$ increases monotonically towards unity with increase of c. Using the same reduction factor for both J^{zz}_{Co-Co} and
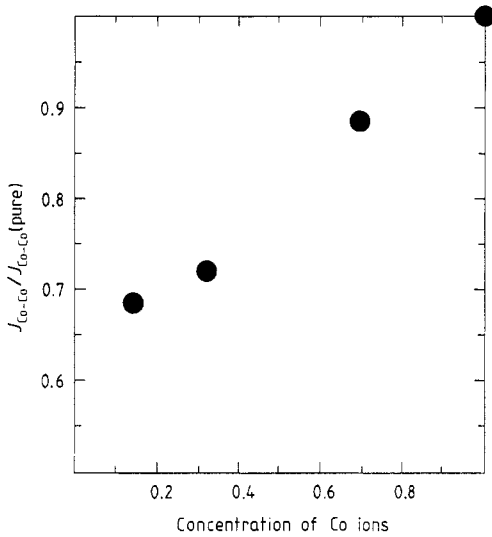
Figure 5. The modification factor for J_{Co-Co} determined by observed spin-wave dispersion relations as a function of Co^{2+} concentration.
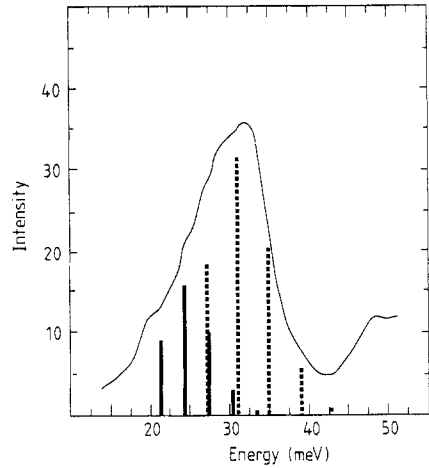

Figure 6. Ising energy levels and their relative intensities calculated with the use of modified J_{Co-Co} ($c = 0.7$; $\zeta_a = 0.47$): ——, observed and smoothed spectrum. The intensity ratio of the Co mode (group of broken bars) to the Ni mode (group of solid bars) is arbitrarily determined.

J_{Co-Co}^{xx}, it was found that $J_{Co-Co}^{\alpha\alpha}$ ($\alpha\alpha = zz.xx$) is 0.69, 0.71 and 0.88 of the pure crystal value for $c = 0.14, 0.32$ and 0.7, respectively. At the zone boundary, it is believed that the structure in the excitation spectrum can be described by the Ising cluster model (Buyers *et al* 1971). When the modified J_{Co-Co} is used in the calculation of the Ising energies, the observed zone boundary spectrum is reproduced well, as shown in figure 6. It should be noted that the excitation energy at the zone boundary in our expression of the dispersion relation corresponds to the averaged energy of these Ising excitations.

The large reduction in the exchange parameter between Co ions in the mixed crystal may be attributed mainly to the complicated behaviour of Co ions in a crystal field. The cubic octahedral crystal field (ignoring the small tetragonal distortion of the octahedron) splits the ^4F ground term of Co^{2+} into two orbital triplets T_1 and T_2 and a singlet A_2. The lowest triplet T_1 is split by the spin–orbit interaction, and the $j = \frac{1}{2}$ Kramers doublet is given as the lowest state. In previous studies, the exchange parameters J_{Co-Co} were effectively deduced from the $S' = \frac{1}{2}$ model, i.e. the two-level model. It should be noted that in this mixed system the exchange field acting on Co^{2+} ions varies considerably with variation in c and that the variation in exchange field can affect the mixing of higher energy levels. As discussed in a detailed analysis of excitations in cubic perovskite ($KCoF_3$) by Buyers *et al* (1971), the influence of higher energy levels must be taken into consideration properly.

The Hamiltonian which describes the single-ion state of a Co^{2+} ion in the antiferromagnetic state may be written

$$H_0 = H_{cf} + H_{s-o} + H_{mf} \tag{1}$$

where the first term and the second term describe the crystal field and the spin–orbit

coupling, respectively. The third term—the molecular-field part of the exchange energy—is

$$H_{mf} = H_z S_{Co}^z$$

$$H_z = 8J_{Co-Co}^{zz} \langle S_{Co}^z \rangle + 8(1-c)(J_{Co-Ni}^{zz} \langle S_{Ni}^z \rangle - J_{Co-Co}^{zz} \langle S_{Co}^z \rangle). \qquad (2)$$

At low temperatures, $\langle S_{Co}^z \rangle$ and $\langle S_{Ni}^z \rangle$ are 0.5 and 1, respectively. The energies of states in the antiferromagnetic state, which can be obtained from the Hamiltonian (1), depend on c. The exchange field for Co^{2+} spins in the mixed crystal is stronger than that in the pure Rb_2CoF_4 and, even if the exchange interaction between real Co^{2+} spins remains unchanged, the exchange parameter projected on to the $S' = \frac{1}{2}$ model may be modified. A similar calculation of spin waves which has been carried out for $KCoF_3$ (Buyers *et al* 1971) and in which the excitations to the higher energy levels over the lowest doublet are included will be possible. However, relevant matrix elements were not calculated for our system because there are still unknown factors such as the magnitude of the spin–orbit interaction or the degree of contribution from the variation in the lattice parameter to the superexchange interaction between real Co^{2+} spins.

In the above discussion, we gave a possible explanation for the observed concentration dependence of the spin-wave dispersion relations on the basis of a simple mean-crystal model. However, to elucidate and understand the spin dynamics of random magnets in more detail, an improved theory which takes into account the effects of correlations between spins not only on the spin-wave dispersion but also on the lineshape of spectrum in the calculations is needed.

4. Conclusion

Assuming that only the value of J_{Co-Co} is affected by the concentration of Co^{2+} ions and that the empirical relation of the exchange interaction parameter between Co and Ni spins is still valid, we have shown that the mean-crystal model is able to represent the dispersion relations of excitations in $Rb_2Co_cNi_{1-c}F_4$ and that the Ising cluster model is also able to describe the zone boundary response. The reduction factor for J_{Co-Co} was determined experimentally as a function of c. The large reduction in J_{Co-Co} in the mixed crystal may be attributed mainly to the change in the single-ion state of the Co ion which is in a distorted octahedral crystal field and perturbed by a spin–orbit interaction. More detailed information such as optical spectroscopy data will be necessary in order to confirm the consistency between observed concentration dependences of the dispersion relations and the many-level model which includes the mixing of higher energy levels over the lowest doublet. It will also be necessary to improve the mean-field type of theory and to compare not only the dispersion relations but also the lineshape of the spectrum, to achieve a more unambiguous understanding of spin dynamics in random magnets.

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