Optical Spectroscopy of Mixed Metamagnetic $Fe_xCo_{1-x}Cl_2$ Crystals

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Electronic absorption spectra are reported for single crystals of composition $Fe_xCo_{1-x}Cl_2$ as a function of temperature from 300 K to 4 K. A broad band at 436 nm is assigned to Fe(II) → Co(II) charge transfer and the temperature dependence of its intensity is related to the magnetic exchange between the ions. The $^2T_{1g}(^2H)$ excitation of Co(II) in the mixed crystals has an unusual temperature dependence which correlates with the Néel temperature.

1. Introduction

In recent years solid state physicists have shown a strong interest in the behaviour of mixed magnetic crystals, that is, solid solutions containing two different transition metal or lanthanide ions isomorphously substituting for one another in the same lattice [1]. To understand the properties of the mixture fully one has to assume that the substitution is purely random or in other words that the two components form an ideal solid solution. Clearly there is no such thing as a solid solution which is truly ideal on the atomic level so one must try to find systems which approach it as closely as possible. Neighbouring transition elements whose radii differ only slightly are obvious candidates, and a further element of interest is added when the two ions have ground states which result in competing single ion anisotropies. Two such ions are Fe(II) and Co(II) in the form of their dihalide salts. Their ionic radii differ only by 4%. Moreover $FeCl_2$ and $CoCl_2$ both crystallize with the space group D_{3d}^5 and with lattice parameters, respectively, $a = 3.603, 3.553$; $c = 17.536, 17.359$ Å [2]. This paper reports the preparation, characterization and optical spectroscopy of mixed crystals $Fe_xCo_{1-x}Cl_2$. The ligand field spectra appearing in the visible region are a convenient probe of the magnetic properties of the mixture since for both ions they are of spin-forbidden type and gain their intensity by coupling with thermally populated spin waves.

In both compounds the metal ion is subjected to a crystal field of predominantly octahedral symmetry but with a small trigonal component. Both the cubic field ground state of Fe(II) ($^5T_{2g}$) and of Co(II) ($^4T_{1g}$) are also split in first order by spin-orbit coupling, of magnitude somewhat greater than the trigonal field. The net result is that for Fe(II) the "J" = 1 lies lowest, and is further split by the trigonal field into a lower $M_J = 0$ and an upper $M_J = \pm 1$ separated by about 17 cm^{-1} [3]. For Co(II), on the other hand, the ground state is "J" = $\frac{1}{2}$ which, being a Kramers doublet, cannot be split further by the trigonal field. Because of this difference in their ground states the magnetic structures of $FeCl_2$ and $CoCl_2$ are quite different: in $FeCl_2$ the spins are aligned parallel to the hexagonal axis while in $CoCl_2$ they lie in the basal plane [4]. Thus in mixed crystals there is competition between the respective single ion anisotropies, which will align the Fe(II) and Co(II) spins in orthogonal directions, and the Fe-Co exchange, which will tend to make them parallel.

2. Experimental

a) Crystal Growth

$FeCl_2$ was synthesised from Specpure Fe metal and HCl gas and $CoCl_2$ by dehydrating the Analar grade hydrate. Both were further purified by sublimation in a stream of HCl gas. The $FeCl_2$ was tested for traces of Fe(III) with thiocyanate but none was found. In a nitrogen filled glove bag, appropriate proportions of the two powdered compounds were loaded into fused silica ampoules 1 cm diameter and about 15 cm long, one end of which had been extended to a fine point. The ampoules were sealed with a tap inside the glove bag, transferred to a vacuum line, evacuated to 10^{-6} torr, flared out and sealed. The melting points of $FeCl_2$ and $CoCl_2$ are

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respectively 672 and 735 °C, so the ampoules were heated to 750 °C in a muffle furnace and agitated to ensure the molten contents were thoroughly mixed. After cooling they were transferred to a Metals Research BCG crystal growing furnace, heated again to 750 °C and lowered at 3 mm per hour through a temperature gradient, followed by slow cooling to room temperature.

Table 1 lists the concentrations of all crystals grown as part of this programme. All were optically homogeneous under the microscope and boules up to 1 cm and several cm long were obtained in many cases. Samples from the top and bottom of each boule were analysed for Fe and Co by atomic absorption spectroscopy, with the results shown in Table 1. The small variation down the boules is a further indication of their homogeneity. However, to take account of such small variations as do exist, a piece taken from the actual crystal section used for each spectroscopic experiment was also analysed separately. In addition to the experiments reported here, crystals from this set have been used for light scattering measurements of tricritical behaviour [5], and both elastic and inelastic neutron scattering studies of the variation of Néel temperature and spin wave excitations with composition [6].

b) Optical Spectroscopy

Absorption spectra in the visible and near ultraviolet were recorded using a McPherson RS10 high resolution double beam spectrophotometer equipped with an Oxford Instruments CF100 continuous flow helium cryostat. Samples were mounted in vacuo on a copper block with Cryocon copper conducting grease in good thermal contact with a CLTS temperature sensor attached to an Oxford Instruments temperature controller. We estimate that the precision of temperature measurement was about ± 0.5 K and the stability about ± 0.1 K. All spectra reported here were recorded with the incident light propagating parallel to the c-axes of the samples (axial orientation).

Table 1. Chemical analyses (x) of $Fe_xCo_{1-x}Cl_2$ crystal boules.

Top		Bottom	
Fe	Co	Fe	Co
0.23	0.77	0.19	0.81
0.40	0.60		
0.61	0.39	0.62	0.38
0.69	0.31	0.62	0.38
0.71	0.29		
0.73	0.27		
0.75	0.25	0.69	0.31
0.76	0.24		
0.78	0.22	0.74	0.26
0.88	0.12	0.86	0.14
0.93	0.07	0.89	0.11
0.95	0.05	0.94	0.06
0.98	0.02		
0.99	0.01		

3. Results

Two spectral regions in the visible and near ultraviolet were examined in detail. In $CoCl_2$, as well as solid solutions with diamagnetic hosts such as $CdCl_2$, a sharply structured band system between 510 and 530 nm has been assigned to $^2T_{1g}(^2H)$. The behaviour of the zero-phonon line in this region is diagnostic of pair and higher cluster formation in dilute solid solutions of this and the corresponding bromide [7]. On the other hand the $FeCl_2$ absorption spectrum contains a highly structured band system near 327 nm, most probably assigned as $^3T_{1g}(^3H)$, whose variation with temperature and applied magnetic field has provided a sensitive probe of spin correlations in that compound [8]. Our aim was to examine the behaviour of both band systems in the $Fe_xCo_{1-x}Cl_2$ mixed crystals. However, the 427 nm region was covered by a new broad absorption not present either in $FeCl_2$ or $CoCl_2$.

a) 350 – 500 nm Region

Figure 1 shows the absorption spectra of $FeCl_2$, $CoCl_2$ and a crystal containing 40% Fe and 60% Co, all at 4.2 K. In addition to the weak spin-forbidden ligand field bands, each of the pure dihalides has a sharp absorption cut-off, in $FeCl_2$ at 395 nm and in $CoCl_2$ at 345 nm. Mixed crystals have similar absorption edges at wavelengths varying between these two extremes but, surprisingly, they also have a further broad band centred at 435 nm. Chemical analysis shows that it is not due to adventitious impurities such as Fe(III). Following the integrated area under this band at 80 K as a function of composition we find that it varies approximately as $x(1-x)$, with maximum intensity near 50:50 composition.

Remarkably, the integrated area of the 435 nm band also increases quite markedly with decreasing temperature, as shown in Figure 2. The insert in

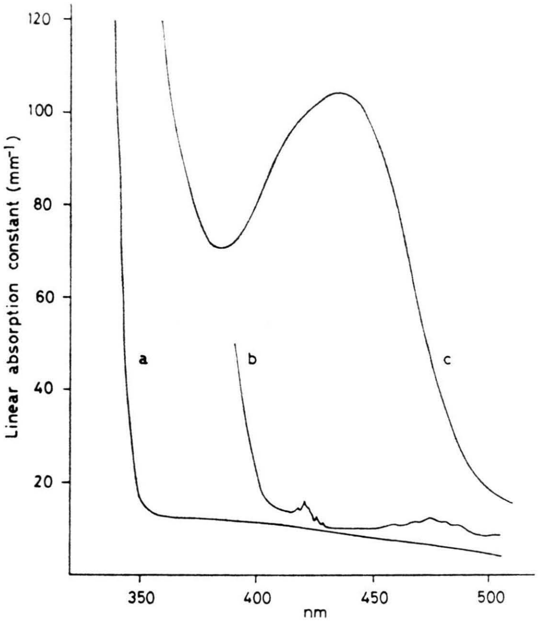

Fig. 1. Near ultraviolet spectra of (a) $CoCl_2$, (b) $FeCl_2$ and (c) $Fe_{0.40}Co_{0.60}Cl_2$ at 80 K.

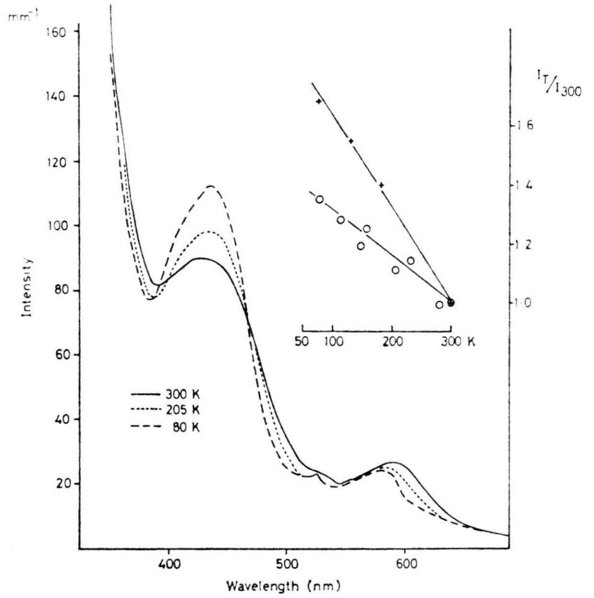

Fig. 2. Temperature variation of near ultraviolet band in $Fe_{0.40}Co_{0.60}Cl_2$; inset, intensity versus temperature for $Fe_{0.40}Co_{0.60}Cl_2$ (o) and $Fe_{0.23}Co_{0.77}Cl_2$ (x).

that Figure reveals that the extent of the increase varies somewhat with composition while in the spectra themselves the behaviour of the 435 nm band contrasts very clearly with that of the band near 600 nm, principally due to the $^4T_{1g}(^4P)$ ligand field transition of Co(II). The latter decreases in intensity with decreasing temperature in the way one expects for a vibronically assisted transition.

b) 510 – 530 nm Region

Absorption spectra from 510 – 530 nm are shown in Fig. 3 for $CoCl_2$ and three different solid solutions with Fe. For $CoCl_2$ and $Fe_{0.40}Co_{0.60}Cl_2$ spectra are only reported at 7 K while for $x = 0.62$ and 0.70, spectra at several temperatures are shown. In most of their more obvious features the spectra of the mixed crystals are essentially a superposition of bands which can be traced back to the two pure materials. For example the weak band near 532 nm and the much more intense one peaking at 526 nm represent respectively the zero-phonon band and phonon-sideband of $^2T_{1g}(^2H)$ of Co(II), phile most of the bands between 510 and 520 nm arise from Fe(II). Quantitatively, the peak linear absorption constant at 526 nm is almost exactly a linear function of Co(II) concentration across the series.

Temperature dependence experiments in this region focussed on the 532 nm band, with results shown in Fig. 4 for the $x = 0.70$ crystal. The band remains observable up to at least 100 K before broadening and coalescing into the more intense sideband. Below about 30 K its halfwidth is almost constant, but it shifts monotonically with increasing temperature from 532.0 to 532.7 nm. By comparison, in the crystal with $x = 0.895$ the corresponding band shifts from 531.8 nm at 5.5 K to 537.8 nm at 90 K.

In contrast to the monotonic behaviour of its frequency and halfwidth as a function of temperature, the intensity of the 532nm band varies in quite a remarkable fashion. As Fig. 5 indicates for crystals of three different compositions, the area of the band first increases rapidly with increasing temperature and then reaches a maximum, most sharply defined in the crystal containing the least Co(II), followed by a steady fall. To our knowledge such a strikingly non-monotonic variation of a ligand field band has never been observed before.

The variation of the spectrum with applied magnetic field both parallel and perpendicular to the c-axis was also studied at 4.2 K for the $x = 0.99$ crystal. In this crystal the 532 nm band is already split into three closely spaced components in zero field (532.35, 532.60 and 532.95 nm). With $H \| c$

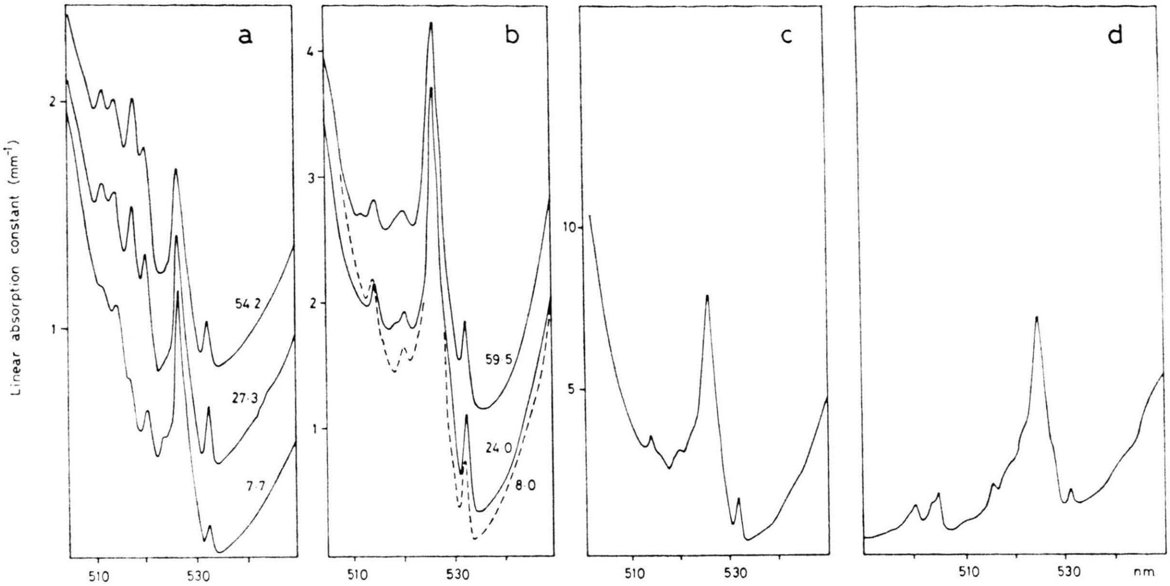

Fig. 3. 510—530 nm region in (a) $x = 0.895$, (b) $x = 0.62$, (c) $x = 0.40$, (d) $CoCl_2$.

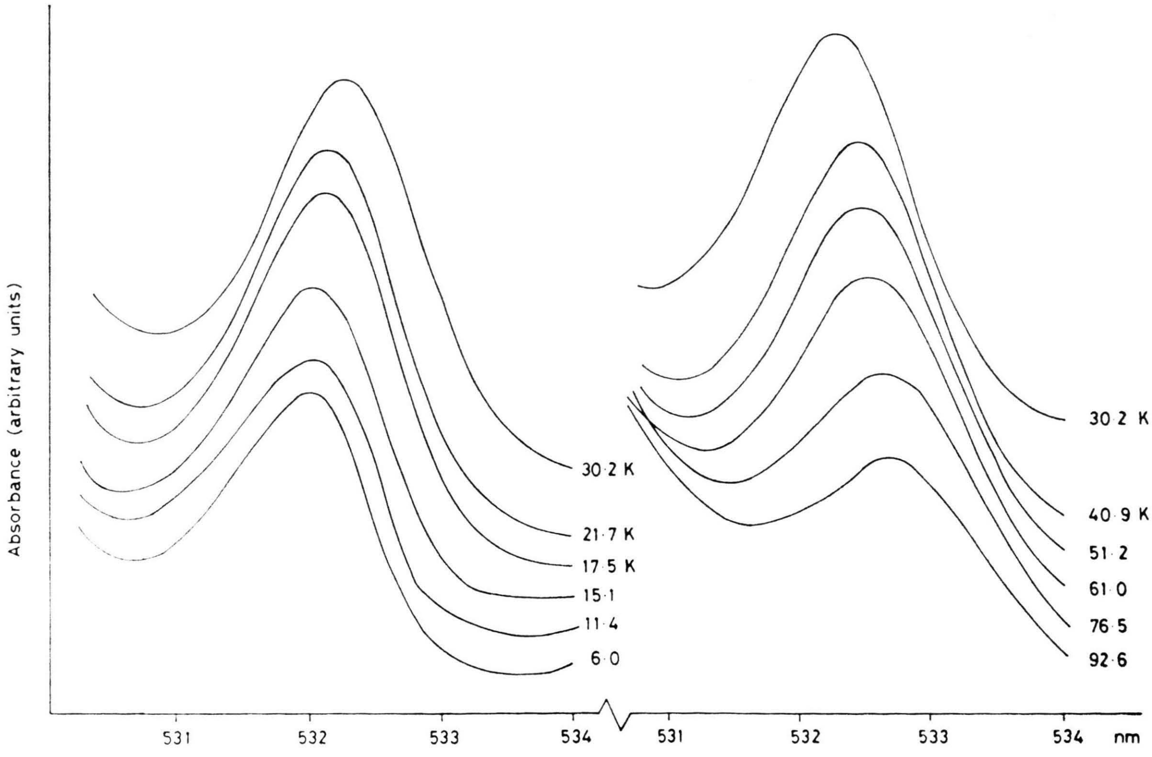

Fig. 4. 532 nm band in $Fe_{0.70}Co_{0.30}Cl_2$ at various temperatures.

of 5 Tesla the two shorter wavelength bands move about 0.08 nm to the blue while the longest wavelength component remains stationary. Fields parallel to *c* up to 3 Tesla, on the other hand, cause the two longest wavelength bands to shift 0.10 nm to the blue, the third remaining constant.

4. Discussion

a) Near Ultraviolet Band

Since this band does not appear in the spectra of $FeCl_2$ or $CoCl_2$, but only in $Fe_xCo_{1-x}Cl_2$, it must result from a transition involving both ions. Further confirmation that it is an interionic transition comes from the concentration dependence of the intensity, which varies roughly as the product of the concentrations of the two kinds of ion. The most probable assignment is as a metal-to-metal charge transfer excitation. Other than in mixed valency compounds [9] examples of such transitions are quite rare, though we note that a similar assignment has been given to a near ultraviolet band in $KZnF_3$ simultaneously doped with Cu(II) and Mn(II) [10]. A simple argument involving the relevant gas phase ionization potentials and electron affinities of Fe^{2+} and Co^{2+} suggests that the charge transfer should be from Fe(II)→Co(II) in the crystal. That the band is relatively weak (peak linear absorption constant about $100-150\,\text{mm}^{-1}$) also argues in favour of the intervalence charge transfer assignment since the overlap between partly occupied 3 d shells on neighbouring metal ions via intervening chloride ions will certainly not be large.

A feature requiring special comment is the increase in intensity of the band as the temperature is lowered. Quite often the intensities of ligand-to-metal charge transfer bands rise by a few percent on cooling from room temperature to 4 K because the lattice contraction improves overlap between the donor and acceptor orbitals. Such an effect may be operating in the present case but the increase is much more marked: the area of the band in the $x=0.23$ crystal increases at least 60% from room temperature to 80 K for example, which is much too large to be accounted for by lattice effects. An alternative explanation is that the magnetic exchange interaction influences the probability of the metal-metal charge transfer. Cox [11] pointed out recently that in a mixed valency compound, such as one containing Fe(II) and Fe(III) both in high spin states, the transition electric dipole matrix element for electron transfer between the two ions depends on the exchange coupling between them. Pictorially, this arises from the fact that an electron transferred without change of spin orientation can only enter an orbital on the other metal if it is either empty or singly occupied by an electron with the opposite spin orientation. The Russell Saunders ground term of Fe(II) in an octahedral site is $^5T_{2g}$ while that of Co(II) is $^4T_{1g}$. Removing an electron from Fe(II) increases its spin from $S=2$ to $5/2$, and replacing it on Co(II) reduces it from $S=3/2$ to 1. Consequently to the extent that the ground state of the pair is saturated ferromagnetically the transition probability is increased or, if the coupling is antiferromagnetic, it will be reduced. The populations of the exchange split levels within the ground state vary with the temperature and hence so will the oscillator strength of the absorption band. Now the nearest neighbour exchange interactions in $FeCl_2$ and $CoCl_2$ are both ferromagnetic, the constants being respectively 7.88 [3] and 14.25 K [12]. It is customary to assume that the constant J_{AB} describing the interaction between two dissimilar ions is the geometric mean of J_{AA} and J_{BB} which in the present case is also ferromagnetic. Therefore we expect the area of the metal-metal charge transfer band to increase with decreasing temperature, as observed. The anticipated effect is of the right magnitude but unfortunately quantitative comparison of theory with experiment is rendered difficult by the nature of the two single ion ground states.

Cox's model takes no account of orbital angular momentum, and assumes that the states of the two ions can be classified simply by S, M_S. As explained in the Introduction $^5T_{2g}$ and $^4T_{1g}$ are split in first order by the spin-orbit interaction to yield, in both cases, manifolds of states extending over $300-400\,\text{cm}^{-1}$. Adding a trigonal field and the exchange perturbation produces further splittings so that the final temperature variation is determined by summing over a very large number of levels. Although the energies of a lot of these levels have been located in related systems such as $Fe_xMn_{1-x}Cl_2$ by Raman scattering there is not sufficient data about the ground state manifold in the $Fe_xCo_{1-x}Cl_2$ system to justify an attempt to fit the temperature dependence of the ultraviolet band to a more elaborate version of Cox's model, taking into account spin-orbit coupling.

b) 510 – 530 nm Region

It is now well established that the electric-dipole intensity of spin-forbidden ligand field transitions in the metamagnetic 3 d dihalides is dominated by processes in which creation of an exciton is accompanied by annihilation of a thermally populated magnon propagating within the ferromagnetic layers [13]. Such combination bands therefore have intensities which are very temperature dependent: they behave as "hot" bands. The detailed form of the temperature variation depends on the magnon density of states (and hence on the exchange Hamiltonian) and on the presence or absence of a gap in the magnon spectrum at the zone centre, i. e. on the single-ion anisotropy. In this respect FeCl_2 mimics a two-dimensional Ising ferromagnet with a large anisotropy while CoCl_2 is an XY-system with large anisotropy. Thus the 427 nm band in FeCl_2 obeys an intensity law $T^2 \exp(-E(\mathrm{o})/kT)$, where $E(\mathrm{o})$ is the zone centre gap, and the 532 nm band in CoCl_2 would be expected to vary as T^3, similar to that followed by the analogous band in CoBr_2 [8]. Neither of these functions in any way resembles the temperature variation of the 532 nm band shown in Figure 5. Quite unprecedented, indeed, is the appearance of a maximum in the intensity *vs* temperature plot.

The vertical arrows in Fig. 5 represent the Néel temperatures of the mixed crystals, determined by observing the $(10\bar{1})$ magnetic reflection in the single crystal neutron diffraction as a function of temperature [6]. Clearly there is an excellent correlation of T_N with the temperature at which the variation in optical intensity changes sign, so two types of process must be invoked. Below T_N a "hot" band mechanism is operating while above it a "cold" band mechanism dominates. This change in mechanism is most marked in the $x = 0.99$ crystal for which the maximum at 23 K appears as a sharp cusp. At the same time it is important to note that no other property of the band, such as peak wavelength or halfwidth, undergoes any discontinuity on passing through T_N.

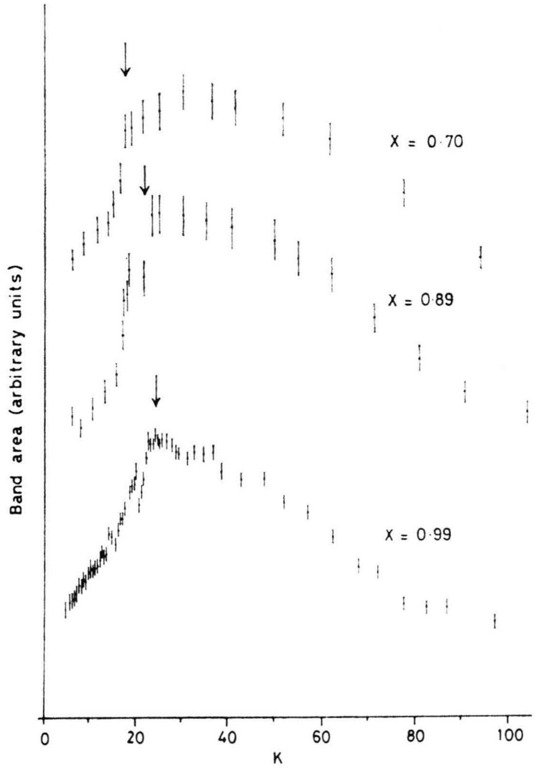

Fig. 5. Temperature variation of intensity of 532 nm band. Arrows indicate Neel temperatures.

In the crystal containing only 1% Co, more than 90% of the Co ions should be present as isolated ions, surrounded entirely by Fe, if there is a completely random distribution. The simplest hypothesis, therefore, is that the E_g' ground state of a single Co(II) is subjected to the exchange field prevailing in FeCl_2, which is quite compatible with the shift of the 532 nm Co(II) excitation to higher frequency (35 cm^{-1}) from the fully magnetized (4 K) to unmagnetized (90 K) state. However, an assumption that the single ion excited state simply couples to the unperturbed magnon spectrum of FeCl_2 fails to reproduce the observed temperature variation of intensity below T_N. Plotting $(\ln I_\mathrm{T} - 2 \ln T)$ where I is the intensity, versus $1/T$ should yield a straight line of slope $E(\mathrm{o})$, as for FeCl_2 itself, but the value of $E(\mathrm{o})$ derived in this way is negative. On the other hand a log-log plot of $(I_\mathrm{T} - I_{4.2})$ versus T is a straight line of slope 1.98 from 4.2 to 23 K. No doubt, therefore, the interaction is not with the unperturbed magnons but with cluster modes involving Fe adjoining the impurity Co. Antiferromagnetic resonance spectra would be needed to identify such modes, as has been dane in $\mathrm{Co}_x\mathrm{Mg}_{1-x}\mathrm{Cl}_1$[14].

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[1] e.g. L. Bevaart, E. Frikkee, J. V. Lebesque, and L. J. de Jongh, Solid State Commun. **25**, 539, 1021 (1978); T. Tawaraya and K. Katsumata, Solid State Commun. **32**, 337 (1979).

[2] M. K. Wilkinson, J. W. Cable, E. O. Wollam, and W. C. Koehler, Phys. Rev. **113**, 497 (1959).

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

[4] C. Starr, F. Bitter, and A. R. Kaufmann, Phys. Rev. **58**, 977 (1940).

[5] T. E. Wood and P. Day, J. Magn. and Magn. Mater. **15–18**, 782 (1980).

[6] T. E. Wood, K. R. A. Ziebeck, and P. Day, to be published.

[7] A. Bailey, D. J. Robbins, and P. Day, Mol. Phys. **28**, 1519 (1974); I. W. Johnstone, K. J. Maxwell, and M. G. Read, J. Magn. and Magn. Mat. **15–18**, 819 (1980).

[8] D. J. Robbins and P. Day, J. Phys. **C 9**, 867 (1976).

[9] M. B. Robin and P. Day, Adv. Inorg. Chem. Radiochem. **10**, 247 (1967).

[10] J. Ferguson, H. J. Guggenheim, and E. R. Krausz, J. Phys. **C 4**, 1866 (1971).

[11] P. A. Cox, Chem. Phys. Letters.

[12] M. T. Hutchings, J. Phys. **C 6**, 3413 (1973).

[13] P. Day, Collogues Int. C.N.R.S. **255**, 237 (1977).

[14] M. C. K. Wiltshire, J. Phys. **C 12**, 3571 (1979).