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**Abstract.** In this work Mössbauer spectra of CsCo$_{1-x-y}$$^{57}$Fe$_x$Mg$_y$Cl$_3$ (where $x \sim 1\%$ and $y = 0.07, 0.3, 0.7, 2.6\%$) in powdered form have been taken for a range of temperatures from 250 K down to 5.5 K. The spectra of these compounds taken below 21 K could be analysed in the same way as the spectra of CsCo$_{0.99}$Fe$_{0.01}$Cl$_3$ where the fits to the spectra are consistent with the magnetic phases of pure CsCoCl$_3$. CsCoCl$_3$ is a one-dimensional Ising-like antiferromagnet and moving domain walls or 'solitons' have been observed in the one-dimensionally ordered Co$^{2+}$ chains from $\sim$75 K down to 9 K. At 9 K full three-dimensional order is formed. However, experiments on Mg-doped CsCoCl$_3$ indicate that the Mg suppresses this transition so that it may be possible for solitons to be present below 9 K. No unequivocal evidence to indicate the presence of solitons below 9 K in Mg-doped CsCoCl$_3$ could be found in the Mössbauer spectra.

It was found that the addition of the Mg lowers the temperature of the transition to the partially disordered phase, $T_{N_1}$, from $21.1 \pm 0.3$ K (no Mg) to $19.6 \pm 0.3$ K (2.6 at.% Mg). The spectra of CsCoCl$_3$ doped with 2.6 at.% Mg showed differences that resulted in soliton relaxation rates which were approximately a factor of two higher than the rates determined for the other compounds. In all compounds the soliton relaxation rates determined above 9 K were found to be between one and two orders of magnitude below the theoretical prediction for a non-interacting soliton gas and it is suggested that this model is not appropriate for CsCoCl$_3$.

## 1. Introduction

CsCoCl$_3$ is a quasi-one-dimensional (1D) Ising-like antiferromagnet and has been widely studied because of its unusual magnetic phases (Mekata and Adachi 1978) and because moving domain walls or 'solitons' have been observed in the antiferromagnetically ordered Co$^{2+}$ chains (Boucher *et al* 1985).

CsCoCl$_3$ is isomorphic to a class of compounds of the type ABX$_3$, where A denotes a large monovalent cation, B is generally a first-row transition metal, and X is usually Cl$^-$ or Br$^-$. The crystal structure consists of a hexagonal close-packed lattice of A and X ions with the B ions occupying the octahedral interstices surrounded by six X ions. Along the $c$-axis (BX$_6$) face-sharing octahedra make infinite chains. This crystal structure—with the large separation between nearest-neighbour B ions in the $a$–$b$ plane ($\sim$7 Å) compared to the B ion separation along the $c$-axis ($\sim$3 Å) (Ackerman *et al* 1974)—gives the magnetic ABX$_3$ compounds their characteristic 1D nature. This 1D magnetic behaviour was discovered by Achiwa (1969) using magnetic susceptibility experiments.

In CsCoCl$_3$ the antiferromagnetic exchange interaction between neighbouring Co$^{2+}$ ions along the $c$-axis (the intrachain interaction) is $\sim$10$^2$ times stronger than the interaction

between $Co^{2+}$ ions in the $a$–$b$ plane (the interchain interaction). Along the $c$-axis CsCoCl$_3$ has spin interactions described by the spin Hamiltonian

$$\mathcal{H} = 2J \sum_i [s_i^z s_{i+1}^z + \varepsilon(s_i^x s_{i+1}^x + s_i^y s_{i+1}^y)] \tag{1}$$

where $J = 75$ K, $\varepsilon = 0.12$, and $s = \frac{1}{2}$ (Achiwa 1969, Tellenbach 1978, Yoshizawa *et al* 1981). Villain (1975) has shown that solutions to this Hamiltonian exist in the form of solitons (or domain walls) with a width of one lattice spacing. These solitons can propagate with constant velocity and are not affected by interactions with other solitons. This is referred to as the non-interaction soliton gas (NISG) model.

As a soliton passes a given site, the spin at that site is 'flipped' with the flipping rate given as a function of temperature $T$ by

$$\Gamma = \frac{4k_B T}{\pi \hbar} \exp(-J/k_B T) \sinh[2\varepsilon J/k_B T] \tag{2}$$

where $J$ and $\varepsilon$ are defined as in equation (1). This unusual dynamic effect was first observed by Adachi (1981) using electron spin resonance (ESR).

Above $\sim 75$ K CsCoCl$_3$ is fully paramagnetic. Below this temperature regions of short-range antiferromagnetic order begin to develop along the $c$-axis with the $Co^{2+}$ spins aligned collinearly along this axis. Solitons provide the mechanism for spin reversal in these chains.

The antiferromagnetic nearest-neighbour interchain interaction causes a magnetic phase transition at $T_{N_1} = 21.2 \pm 0.5$ K (Melamud *et al* 1974, Mekata and Adachi 1978, Yoshizawa and Hirakawa 1979) from the paramagnetic phase to a partially disordered (PD) phase where two-thirds of the $Co^{2+}$ chains become antiferromagnetically correlated in the $a$–$b$ plane. The remaining chains are uncorrelated with the others and are said to be frustrated since they are surrounded by an equal number of spin-up and spin-down nearest neighbours and show only 1D magnetic order with solitons present. The frustrated chains order at $T_{N_2} \simeq 9$ K (Mekata and Adachi 1978) due to a weak next-nearest-neighbour ferromagnetic interchain interaction. These chains correlate with the other ordered chains so that CsCoCl$_3$ is fully three-dimensionally (3D) ordered. Below 9 K then, the magnetic structure of CsCoCl$_3$ consists of an antiferromagnetic stacking of collinear spin planes in which one-third of the spins are aligned in the opposite direction to the others (Melamud *et al* 1974).

The $^{57}$Fe Mössbauer effect provides a frequency window of $10^5$–$10^9$ Hz for studying dynamic effects such as spin fluctuations. In this range of frequencies these effects can be seen in the spectra as changes in line-shape and line position. Mössbauer spectroscopy has been used to study $Fe^{2+}$ substituted for $Co^{2+}$ in CsCoCl$_3$ (Ward *et al* 1987, Mekata 1990). Line broadening observed in spectra taken between 9 K and $T_{N_1}$ has been attributed to soliton relaxation in the disordered chains and $Fe^{2+}$ electronic relaxation in the correlated chains.

The model used by these authors to describe the electronic states of the $Fe^{2+}$ ion is as follows. The $Fe^{2+}$ ion lies in an octahedral site with a small trigonal distortion. The 25 substates of the $^5$D ground state term are split by the octahedral part of the crystal field into an orbital triplet, $T_{2g}$, and an orbital doublet, $E_g$. For $Fe^{2+}$ in CsFeCl$_3$ the $T_{2g}$ orbital triplet lies $\sim 7000$ cm$^{-1}$ below the $E_g$ doublet (Putnik *et al* 1976) and it is expected that $Fe^{2+}$ in CsCoCl$_3$ will have a similar splitting. The orbital wavefunctions appropriate for trigonal symmetry that transform as $T_{2g}$ are

$$x_+ = -\sqrt{2/3}Y_2^{\bar{2}} - \sqrt{1/3}Y_2^1 \qquad x_0 = Y_2^0 \qquad x_- = \sqrt{2/3}Y_2^2 - \sqrt{1/3}Y_2^{\bar{1}}$$

where $Y_l^m$ are spherical harmonics. The degeneracy of the $T_{2g}$ and $E_g$ levels is then removed by the trigonal, spin–orbit, and (below $T_{N_1}$) magnetic exchange interactions. The

arrangement of the lowest three levels when all interactions are included is shown in figure 1. With zero exchange field the ground state is a singlet, principally $|x_0, 0\rangle$ (where $m_s$ in $|x_0, m_s\rangle$ refers to the spin quantum number with $S = 2$). The next-highest energy level is a doublet whose two states have major components $|x_0, +1\rangle$ and $|x_0, -1\rangle$. This level lies $\sim16$ cm$^{-1}$ above the ground state (Ward *et al* 1987). In the presence of an exchange interaction the doublet is split so that at 0 K the ground state is now one of the doublet levels with major component $|x_0, -1\rangle$, the state $|x_0, 0\rangle$ lies 3 cm$^{-1}$ above this, and the third level is 37 cm$^{-1}$ above the ground state.
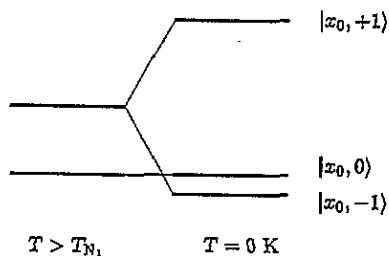


**Figure 1.** The energy level diagram for the three lowest electronic levels for Fe$^{2+}$ in CsCoCl₃. Above $T_{N_1}$ the doublet lies 16 cm$^{-1}$ above the ground state singlet. At 0 K the state with major component $|x_0, -1\rangle$ is 3 cm$^{-1}$ below the singlet.

In fitting the part of the Mössbauer spectrum due to electronic relaxation Ward *et al* (1987) assume that only the lowest two electronic levels are occupied for temperatures below $T_{N_1}$. This is a good assumption for temperatures less than $\sim10$ K so using this model for electronic relaxation for those temperatures will not affect the fitted rates for soliton relaxation.

Mekata *et al* (1987) have reported that doping the diamagnetic ions Mg$^{2+}$ and Zn$^{2+}$ into CsCoCl₃ in low concentrations (<5 at.%) appears to suppress the transition at 9 K so that solitons may be present below 9 K. In the neutron diffraction and magnetic susceptibility experiments the transition to full 3D order could not be found down to 1.6 K, even with impurity concentrations as low as 0.2 at.%.

This paper reports on a Mössbauer study of CsCoCl₃ doped with 1 at.% $^{57}$Fe and Mg in a range of concentrations up to 2.6 at.%. In this work it was hoped to be able to study soliton relaxation below 9 K.

## 2. Experimental details

Mössbauer spectra were taken using a Ranger Scientific MS-900 spectrometer with a VT-900 velocity transducer operating in constant-acceleration mode and a PA-900 proportional counter. The system was used in standard transmission geometry with a moving $^{57}$Co/Rh source at room temperature, and a stationary absorber held at a controlled temperature. The gamma-ray counts were collected over the full cycle of the source movement so the spectra were essentially mirrored about a centre channel. The spectra were computationally folded for analysis and the resulting spectra had flat baselines. The determination of the centre channel for folding, and calibration constants for the spectrometer, was achieved by taking the spectrum of a National Bureau of Standards iron foil.

A Ricor MCH-5B vacuum cryostat was used for cooling the absorber to any temperature between room temperature and $\sim5$ K by drawing a regulated amount of either nitrogen or helium gas from a Dewar of liquid N₂ or He. The temperature was monitored and regulated from the output of a gold/0.07% iron–chromel thermocouple and was stable to $\pm0.3$ K.

Crystals of CsCo$_{1-x-y}$$^{57}$Fe$_x$Mg$_y$Cl₃ (where $x \sim 1\%$, and $y = 0.07, 0.3, 0.7, 2.6\%$) were grown using the Bridgman technique where the constituents are lowered through the

hot zone of a furnace in an evacuated sealed quartz tube. Preparation of the constituents involved mixing stoichiometric amounts of high-purity $CsCl$, $CoCl_2$, and $MgCl_2$ in solution with $^{57}Fe$ dissolved in dilute aqueous HCl and drying the mixture under vacuum. Subsequent analysis of the crystals to determine $^{57}Fe$ and Mg concentration was performed using atomic absorption spectroscopy on a Varian AA-1475 machine. Absorbers were taken from the lower parts of the crystals, and initially samples for analysis were taken from the same regions. When it was found that there were gradients in the Fe and Mg concentrations (samples taken from the top parts of the crystals showed approximately half the amount of Fe and Mg), the actual absorbers used for the Mössbauer experiments were analysed instead. Absorbers were prepared by powdering weighed amounts of the desired crystal, mixing with finely ground boric acid, and pressing the mixture into a steel ring. This procedure was carried out in a dry atmosphere to prevent possible hydration of the absorbers.

## 3. Results: Mössbauer spectra above $T_{N_1}$

The Mössbauer spectra of $CsCoCl_3$ doped with $\sim 1$ at.% $^{57}Fe$, and 0.07, 0.3, 0.7, and 2.6 at.% Mg, above $T_{N_1}$ consist of a quadrupole split pair of absorption lines consistent with the paramagnetic phase of Mg-doped $CsCoCl_3$ (note that here, and in the following discussion, any reference to Mg-doped $CsCoCl_3$ also includes the $\sim 1$ at.% $^{57}Fe$ that was doped into these crystals). The lines are of unequal intensity and this has been attributed to non-random orientation of the crystallites in the powdered absorbers (Ward *et al* 1987). These spectra have been fitted with Lorentzian shaped absorption lines using a least-squares iterative computer routine, and the quadrupole splitting values for these compounds are found to be the same as those for $CsCo_{0.99}Fe_{0.01}Cl_3$. This result is expected since so long as an $Mg^{2+}$ ion is not adjacent to an $Fe^{2+}$ ion along the $c$-axis, then the $Fe^{2+}$ crystallographic site (and hence the quadrupole splitting QS) will not be significantly altered by the presence of the Mg at a low concentration.

   The spectra of $CsCoCl_3$ doped with 2.6 at.% Mg showed (in addition to the main lines) a pair of absorption lines of low intensity situated on the outer wings of each of the main lines. These were also fitted and their area relative to the main lines is consistent with the possibility that they are due to another crystallographic site caused by an $Mg^{2+}$ ion neighbouring an $Fe^{2+}$ ion. The mean ratio of the areas for the left-hand lines is $0.053 \pm 0.010$, and for the right-hand lines it is $0.056 \pm 0.009$. At a given $Fe^{2+}$ site in $CsCoCl_3$ the probability that it will have an $Mg^{2+}$ neighbour is $\sim 2 \times 0.026 = 0.052$ for a Mg concentration of 2.6 at.%. The larger QS observed for this site is consistent with the results of work on Mg-doped $CsFeCl_3$ where the room-temperature QS for the $Fe^{2+}$ ions with $Fe^{2+}$ nearest neighbours is $\sim -1.5$ mm s$^{-1}$, and $\sim -2.5$ mm s$^{-1}$ for the $Fe^{2+}$ ions with one $Mg^{2+}$ neighbour (Lai and Ward 1988).

## 4. Results: Mössbauer spectra below $T_{N_1}$

Shown in figure 2 are representative spectra of the Mg-doped compounds for temperatures below $T_{N_1}$. Note that in figure 2(B) the extra lines discussed above are obscured due to the reduced signal to noise and broadened lines brought about by the magnetic ordering. An initial visual inspection of the unfitted spectra revealed that in all cases the spectra of the Mg-doped compounds were similar to the spectra of $CsCo_{0.99}Fe_{0.01}Cl_3$. As a result, the spectra were initially fitted following the model used by Ward *et al* (1987), and the parameters obtained were investigated for possible effects of the Mg.
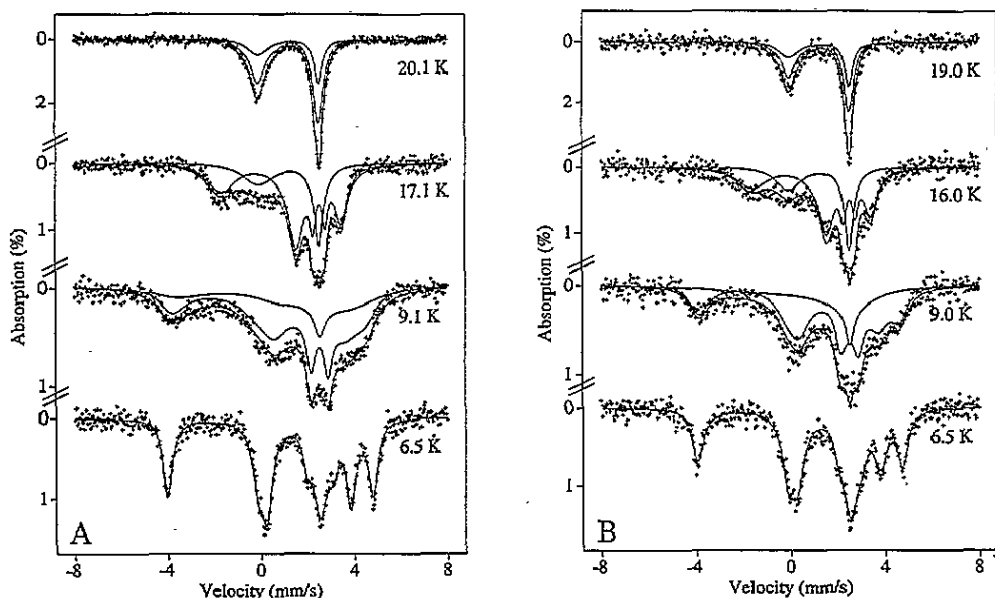
**Figure 2.** Representative low-temperature Mössbauer spectra of (A): CsCoCl₃ doped with 0.07 at.% Mg and $^{57}$Fe and (B): CsCoCl₃ doped with 2.6 at.% Mg and $^{57}$Fe. Below 9 K the solid line is the fit to the data assuming electronic relaxation only. Above 9 K the three solid lines present show the soliton relaxation site, the electronic relaxation site, and the fit obtained by adding these two contributions. The soliton site can be identified as the spectrum with the smallest area.

In the temperature range between 5 K and 21 K relaxation processes occur with times comparable to the $^{57}$Fe excited state lifetime and the spectra are fitted using the stochastic model of Blume and Tjon (1968). Below 9 K where CsCoCl₃ is in the 3D phase the spectra could be fitted to one site with the hyperfine field relaxing slowly between 0 T and ∼24.6 T. This is attributed to electronic relaxation of the $Fe^{2+}$ ion between its lowest two electronic states. Above 9 K where CsCoCl₃ is in the PD phase the spectra could not be satisfactorily fitted to just one site—an additional site was required to obtain an acceptable fit. This additional site has the hyperfine field relaxing between ±∼24.6 T and is attributed to soliton relaxation in one-third of the $Co^{2+}$ chains. When fitting this site, the area was held close to one-third of the total area of the spectrum, consistent with one-third of the $Co^{2+}$ chains containing magnetic solitons.

Figures 3 to 6 show graphs of the parameters obtained from the fits to the spectra. In Figure 3 the hyperfine field for the lowest magnetic electronic level of $Fe^{2+}$ in CsCoCl₃ is shown. The solid line shows the constant field up to $T_{N_1}$ predicted by crystal field theory. Good fits with a constant field could be made up to ∼18 K for all of the compounds, but above 18 K the hyperfine field drops to zero as the temperature approaches $T_{N_1}$. At these higher temperatures the third electronic level will be significantly populated, and the assumption that only the lowest two levels are occupied is not valid. The third level gives a hyperfine field in the opposite direction to the field for the lower level and so a reduction in the fitted hyperfine field may be expected as the third level becomes populated.

If $T_{N_1}$ is defined to be the temperature where the hyperfine field = 0 T, then by extrapolating the points on the graph (figure 3), $T_{N_1}$ is found to be 21.1±0.3 K, 20.5±0.3 K, 20.4 ± 0.3 K, and 19.6 ± 0.3 K for CsCoCl₃ doped with 0, 0.07, 0.7, and 2.6 at.% Mg respectively. The reduction in $T_{N_1}$ with the addition of the Mg is consistent with the theory
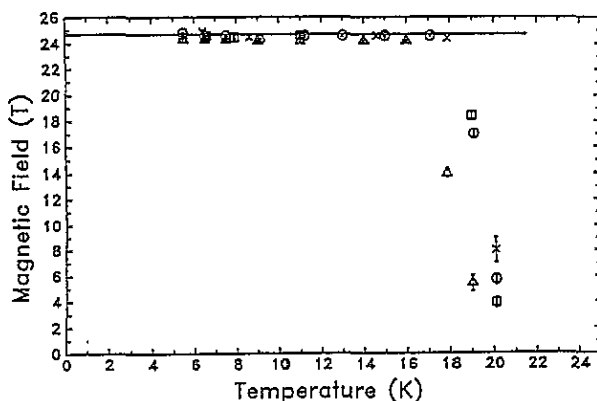
**Figure 3.** Hyperfine field for the lowest magnetic electronic level of $Fe^{2+}$ in $CsCoCl_3$ calculated from fits to the low-temperature spectra of $CsCoCl_3$ doped with $^{57}Fe$ and ×: no Mg, ○: 0.07 at.% Mg, □: 0.7 at.% Mg, and △: 2.6 at.% Mg. The solid line shows the constant field produced by the magnetic electronic level.
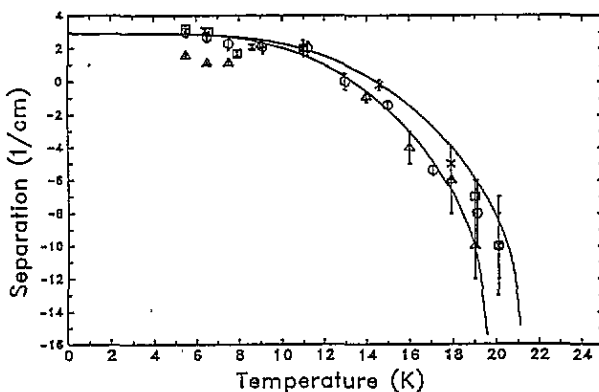


**Figure 4.** Separation of the lowest two electronic levels of $Fe^{2+}$ in $CsCoCl_3$ calculated from fits to low-temperature spectra of $CsCoCl_3$ doped with $^{57}Fe$ and ×: no Mg, ○: 0.07 at.% Mg, □: 0.7 at.% Mg, and △: 2.6 at.% Mg. The solid lines show the theoretical predictions assuming an $S = \frac{1}{2}$ Brillouin function for the effective field for $T_{N_1} = 21.2$ K and 19.6 K.

of Imry *et al* (1975) and Hone *et al* (1975) and agrees with the neutron scattering experiments in which $T_{N_1}$ is found to be 19.8 K for $CsCoCl_3$ doped with 1.7 at.% Mg (Mekata 1990).

Figure 4 shows the energy separation of the two lowest electronic states as deduced from the fits to the spectra of $CsCoCl_3$ doped with the different Mg concentrations. The solid lines show the model predictions which are calculated with $S = \frac{1}{2}$ Brillouin functions for the effective field with $T_{N_1} = 21.2$ K and 19.6 K. The Brillouin function is predicted by mean field theory to be the form of the effective field at the $Fe^{2+}$ site brought about by the exchange interactions in the ordered state. The curve calculated with $T_{N_1} = 21.2$ K is appropriate for the spectra of $CsCo_{0.99}Fe_{0.01}Cl_3$, while the lower curve calculated with $T_{N_1} = 19.6$ K is for the spectra of $CsCoCl_3$ doped with 2.6 at.% Mg. The intermediate concentrations of Mg lie between these ranges. As can be seen the experimentally determined energy separations follow the theoretical predictions fairly closely.

The behaviour of the electronic relaxation rate parameter is shown in figure 5 where it
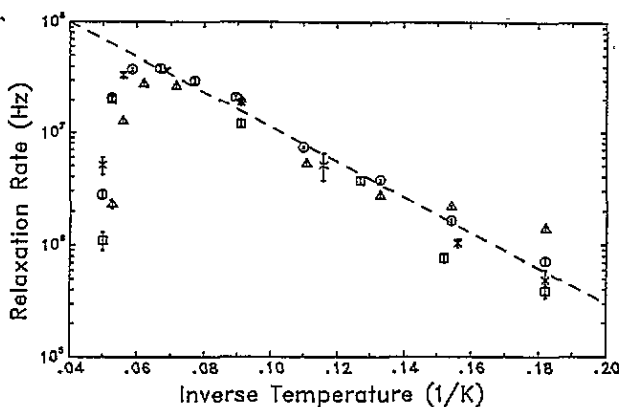
**Figure 5.** Electronic relaxation rates between the lowest two electronic levels of $Fe^{2+}$ in CsCoCl₃ calculated from fits to the low-temperature spectra of CsCoCl₃ doped with $^{57}Fe$ and ×: no Mg, ◯: 0.07 at.% Mg, □: 0.7 at.% Mg, and △: 2.6 at.% Mg. The dashed line is the line of best fit to the 0.07 at.% Mg data below ~15 K.
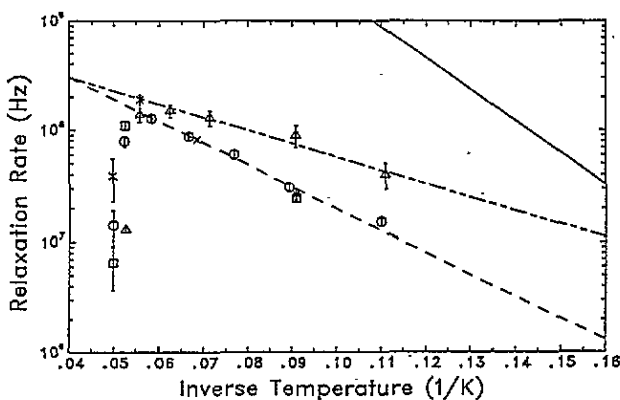


**Figure 6.** Soliton relaxation rates in the magnetic chains of CsCoCl₃ calculated from fits to the low-temperature spectra of CsCoCl₃ doped with $^{57}Fe$ and ×: no Mg, ◯: 0.07 at.% Mg, □: 0.7 at.% Mg, and △: 2.6 at.% Mg. The solid line is the theoretical prediction of the NISG model and the dashed lines are the lines of best fit to the 0.07 at.% Mg and 2.6 at.% Mg data below ~18 K.

is plotted against inverse temperature. The behaviour is similar for each series of results. The dashed line is the line of best fit to the results obtained below ~15 K for CsCoCl₃ doped with 0.07 at.% Mg. It has a slope of $(37 \pm 2)$ K over this temperature range. The deviation of the data from the straight line that occurs as the temperature approaches $T_{N_1}$ is probably a consequence of the two-level model assumptions becoming invalid at these temperatures. The fact that the data follow a straight line when plotted in this manner is evidence that the electronic relaxation is occurring by the Orbach process. In this process transitions between two levels lying close together occur by excitation to a higher-lying third level, and then decay to the other low-lying level. If the third level lies at an energy $\Delta$ (in K) above the ground state then the relaxation rate is given as $\Gamma = k\Delta^3 \exp(-\Delta/T)$ where $k \simeq 10^4$ K$^{-3}$ s$^{-1}$ (Abragam and Bleaney 1970). For $Fe^{2+}$ in CsCoCl₃ the third level is predicted from the results of crystal field fits to lie at ~50 K. So although this is not in perfect agreement with the slope of 37 K, it is still a good indication that this may be the

mechanism for the electronic relaxation.

**Table 1.** Slopes of the lines of best fit to the soliton relaxation rates below 18 K presented in figure 6.

| Mg conc. (at.%) | Slope (K) |
|---|---|
| 0 | $53 \pm 8$ |
| 0.07 | $45 \pm 5$ |
| 0.7 | Insufficient data |
| 2.6 | $28 \pm 9$ |

Figure 6 shows the behaviour of the soliton relaxation rate plotted against inverse temperature. The solid line is the prediction of the NISG model given by equation (2) with $J = 75$ K and $\varepsilon = 0.12$. The dashed lines are the lines of best fit to the 0.07 at.% Mg and 2.6 at.% Mg data below $\sim$18 K. The slopes for the lines of best fit to all of the data below 18 K are shown in table 1. These slopes give a measure of the intrachain exchange constant, $J$, for each compound. The uncertainties in the measured slopes are large but there is a consistent decrease in slope as the Mg concentration increases. In addition to the change in slope, the 2.6 at.% Mg data have soliton rates approximately a factor of two higher than the lower Mg concentrations.

In a recent publication Sheen and McCann (1995) have analysed the spectra of $CsCo_{0.99}Fe_{0.01}Cl_3$ (no Mg) using a two-level model and a three-level model. Their results for the two-level model differ from the results presented here only for the spectrum at 20.1 K which consists of two broadened lines. In fitting this spectrum Sheen and McCann elected to allow the energy level difference to vary and maintain the hyperfine field at 24.8 T. This resulted in a higher soliton rate than reported here. Given that the two-level model is less valid at this temperature and given the featureless nature of the spectrum no importance is placed on this difference in rates.

The model of electronic relaxation involving the three lowest energy levels was developed by Sheen and McCann mainly for use with systems similar to $CsCoCl_3$ but with a higher value of $T_{N_1}$. This model was not applied to Mg-doped $CsCoCl_3$ as the main emphasis was to look at Mg dependent differences in the spectra, especially below 9 K where the two-level model is applicable. At temperatures near $T_{N_1}$ neither the differences in the spectra nor the differences in the soliton rates in $CsCoCl_3$ obtained by Sheen and McCann were sufficient to justify the extra assumptions required by the three-level model.

Mekata (1990) gives the results of soliton flipping rates determined by nuclear magnetic resonance (NMR) and $\mu^+$ spin resonance ($\mu^+$ SR) experiments on pure $CsCoCl_3$, and Mössbauer experiments on $CsCoCl_3$ doped with 3 at.% $^{57}Fe$. The NMR and $\mu^+$ SR results are lower than the theoretical prediction by approximately an order of magnitude (note that in figure 4 of Mekata (1990), the dashed line representing the theoretical prediction has been drawn too low by approximately an order of magnitude). The rates determined from the Mössbauer spectra are similar to those found in this work for temperatures below 17 K and are also between one and two orders of magnitude too low. This indicates that the NISG model does not predict the correct rates for the soliton relaxation processes.

In contrast to the other compounds, $CsCoCl_3$ doped with 2.6 at.% Mg has a density of Mg ions along the $Co^{2+}$ chains that is greater than the soliton density predicted by the NISG model for temperatures below 20 K. This may be why higher soliton relaxation rates are found when fitting these spectra. Boucher (1989) has observed with NMR and neutron spin echo (NSE) experiments a change in the nature of the soliton propagation in the 1D

Heisenberg antiferromagnet $(CD_3)_4NMnCl_3$ when doped with the diamagnetic impurity Cd. The soliton motion is altered from a ballistic motion (constant velocity) to a diffusive motion (displacement $\sim \sqrt{t}$) with the addition of the Cd. Boucher has considered the possibility of a similar effect in $CsCoBr_3$ and $CsCoCl_3$ and has performed NSE experiments on $CsCoBr_3$ doped with 5 at.% Mg. Due to the limited statistical accuracy of the data no definitive conclusions concerning the nature of the soliton propagation could be made. It was reported that the soliton relaxation rate was decreased by a factor of $\sim 20$ at a temperature of 20 K for this compound. In our case an increase in the soliton relaxation rate of a factor of $\sim 2$ is observed for $CsCoCl_3$ doped with 2.6 at.% Mg which is not consistent with Boucher's observations on $CsCoBr_3$.

Results of Mössbauer experiments on other 1D Ising-like antiferromagnets have not been found in the literature. However interesting Mössbauer studies of other types of 1D system doped with a non-magnetic impurity have been carried out on antiferromagnetic $K_2FeF_5$ doped with gallium (Jones *et al* 1989) and on the spin 1 Ising-like ferromagnet $FeCl_2(NC_5H_5)_2$ doped with cadmium (Elmassalami *et al* 1989).

## 5. Discussion

Concerning the magnetic phases of $CsCoCl_3$ doped with Mg, the following conclusion can be made from the results of the fits to the spectra of these compounds: below 9 K the spectra can be fitted satisfactorily to one site with the hyperfine field relaxing between 0 T and $\sim 24.6$ T. Above 9 K it is necessary to fit the spectra to two sites: one site as above, and an additional site with the hyperfine field relaxing between $\pm \sim 24.6$ T.

The additional site is attributed to soliton relaxation, so it was thought that if solitons are present below 9 K in $CsCoCl_3$ doped with Mg, that the spectra would require two sites to fit satisfactorily below 9 K also. From the fits shown this does not seem to be the case. In an attempt to identify any significant differences below 9 K between the spectra of $CsCo_{0.99}Fe_{0.01}Cl_3$ and the spectra of $CsCoCl_3$ doped with Mg, a soliton relaxation site (in addition to the electronic relaxation site) was fitted to the spectra below 9 K. It was found that satisfactory fits could be obtained for the spectra of $CsCoCl_3$ with and without Mg present. The fact that two sites can be fitted to these spectra is not significant because the rate determined for the soliton relaxation is in the region of $10^7$ Hz. For this rate the lines in the spectrum produced are very broad and there are no distinct features. As a result the extra site can be fitted equally well to all the spectra below 9 K. Given these results, a number of reasons as to why the Mössbauer experiments do not show unequivocal evidence of a suppression of $T_{N_2}$ as shown by Mekata *et al* (1987) are considered below.

It is possible that $CsCoCl_3$ doped with $Fe^{2+}$ and $Mg^{2+}$ ions is not a stable system, and that the $Fe^{2+}$ and/or $Mg^{2+}$ ions are not being incorporated into the host crystal in a random manner. However, the ionic radii of $Mg^{2+}$ and $Fe^{2+}$ are within 10% of $Co^{2+}$ (CRC 1990), and the lattice parameters for the corresponding compounds are all within 1% of each other (Soling 1968, Achiwa 1969, Ackerman *et al* 1974), so the dopants should 'fit' into the $CsCoCl_3$ lattice. Experimentally the observed reduction of $T_{N_1}$ and the presence of the weak extra lines in the spectra of $CsCoCl_3$ doped with 2.6 at.% Mg indicate the random substitution of $Co^{2+}$ ions for $Mg^{2+}$ ions.

The model used so far to describe the magnetic phases predicts a sudden transition from the PD phase to the 3D phase at 9 K. This is seen in the results of neutron diffraction experiments (Mekata and Adachi 1978) and neutron scattering experiments (Yoshizawa and Hirakawa 1979). More recent NMR experiments (Kikuchi and Ajiro 1989a), and nuclear spin–lattice relaxation experiments (Ajiro *et al* 1989) indicate that the transition at $T_{N_2}$ may

be gradual rather than abrupt with soliton relaxation processes present below 9 K. From these experiments it is concluded that below ~5 K the $CsCoCl_3$ system is ferrimagnetic, but that as the temperature approaches 9 K spins on one-third of the chains begin to relax slowly due to soliton propagation and as the temperature increases the relaxation rate of the spins increases with the soliton density. In this case the effect of the Mg may be too subtle to be observed with the Mössbauer effect, although the work of Mekata *et al* (1987) certainly indicates that the magnetic ordering processes are altered by the presence of the non-magnetic impurity and it was hoped tht this would be seen as consistent differences in the Mössbauer spectra of $CsCo_{0.99}Fe_{0.01}Cl_3$ and $CsCoCl_3$ doped with Mg.

Finally, it may be that the effect of the $^{57}Fe$ Mössbauer probe needs to be considered more carefully. In this work it has been assumed that the $Fe^{2+}$ ions are magnetically coupled to the $Co^{2+}$ ions and participate in the magnetic order of the crystal. This approach is supported by work on impurity-doped 1D ferromagnets (Elmassalami *et al* 1989) where the Mössbauer experiments show that the magnetic impurities are magnetically coupled in the linear chains as opposed to the non-magnetic impurities which break the chains into segments. However the ESR experiments of Kikuchi and Ajiro (1989b) suggest that doping magnetic $Mn^{2+}$ into $CsCoCl_3$ may have the same effect on the phases as $Mg^{2+}$. If the $Fe^{2+}$ is disrupting the order in the same way, then the addition of Mg may not produce any observable differences in the spectra. To test this theory it would be necessary to perform neutron diffraction and magnetic susceptibility experiments on Fe-doped $CsCoCl_3$ to compare the results with those obtained for the Mg-doped compound. Results of such experiments have not been found in the literature.

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