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1996 J. Phys.: Condens. Matter 8 8407

(http://iopscience.iop.org/0953-8984/8/43/031)

J. Phys.: Condens. Matter **8** (1996) 8407–8412. Printed in the UK

The magnetic susceptibility of the $S = \frac{3}{2}$ finite linear-chain Heisenberg antiferromagnet $CsV_{1-x}Mg_xCl_3$

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Received 10 June 1996, in final form 24 July 1996

Abstract. The temperature-dependence of the magnetic susceptibility of $CsV_{1-x}Mg_xCl_3$ ($x = 0.000$–0.357) is investigated to elucidate finite-size effects in the $S = \frac{3}{2}$ one-dimensional Heisenberg antiferromagnet. The experimental results are compared with the results of the exact-diagonalization method for chains with up to seven-spins.

1. Introduction

One-dimensional (1D) spin systems have been studied for many years. In classical systems, we have exact solutions or good approximations which allow us to perform a quantitative comparison between theory and experiment. In quantum systems, novel effects such as the qualitative difference, suggested by Haldane [1], between integer and half-odd-integer spins with antiferromagnetic interaction have been intensively studied. Not only pure but also impure 1D spin systems have attracted much attention because impurity effects on 1D systems are much more pronounced than are those in two- and three-dimensional (3D) systems. This is because even one impurity breaks the interaction in a 1D system. In theoretical works, Tonegawa *et al* [2] exactly calculated the susceptibility of impure 1D classical Heisenberg chains. Richards [3] extended the calculation to classical chains with $S = \frac{1}{2}$ quantum impurities. In experimental works, $(CH_3)_4NMnCl_3$ (TMMC), a quasi-1D antiferromagnet with $S = \frac{5}{2}$, doped with magnetic or non-magnetic impurities was investigated [3, 4].

In this article, we report the temperature-dependence of the magnetic susceptibility in $CsV_{1-x}Mg_xCl_3$ ($x = 0.000$–0.357), in which the V^{2+} ($S = \frac{3}{2}$) sites of $CsVCl_3$ are replaced in part by non-magnetic Mg^{2+} ions to make finite chains of V^{2+}. $CsVCl_3$ has a hexagonal $CsNiCl_3$ structure with the lattice constants $a = 7.228$ Å and $c = 6.030$ Å and is known to be a fairly good 1D Heisenberg antiferromagnet (HAF) with $S = \frac{3}{2}$ [5, 6]. The chains of V^{2+} ions are aligned along the c axis. The intrachain and interchain exchange coupling constants are estimated to be $J = -115$ K [5, 6] and $J' = -0.046$ K [7], respectively. A 3D long-range ordering has been confirmed below the Néel temperature of 13.3 K [8] (13.8 K [9]). Our principal interest is in elucidating a finite-size effect in $S = \frac{3}{2}$ 1D HAF. Because of the S value being smaller than that of TMMC ($S = \frac{5}{2}$), it is expected that $CsV_{1-x}Mg_xCl_3$ behaves in a more quantum-like manner than does the impure TMMC and shows a reduction in effective spin originating from a quantum effect. We also intend to compare the experimental results with the results of the exact-diagonalization method for

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0953-8984/96/438407+06$19.50

finite chains. In the calculation, the magnetic susceptibility of the $S = \frac{3}{2}$ HAF chain with up to seven spins is evaluated as a function of temperature.

2. Experimental details

The samples of $CsV_{1-x}Mg_xCl_3$ were prepared from a mixture of $CsVCl_3$ and $CsMgCl_3$. The mixture was sealed in an evacuated quartz ampoule and crystallized by the Bridgman method. The obtained product consists of crystals in the form of fine long fibres running parallel to the c axis. The method used to prepare pure $CsVCl_3$ was almost the same as that described by Hirakawa *et al* [8]. The compound $CsMgCl_3$ was synthesized in a quartz tube at 750 °C according to the reaction $CsCl + MgCl_2 \rightarrow CsMgCl_3$. The composition x and the crystal structure were checked by chemical analysis and x-ray diffraction for all the samples.

Using a SQUID magnetometer (Quantum Design MPMS2), the DC magnetic susceptibility was measured for a magnetic field applied parallel and perpendicular to the c axis in the cooling run. The contribution of diamagnetism and Van Vleck paramagnetism was subtracted from the measured susceptibility using diamagnetic susceptibilities of ions given in the literature and the equations expressed by Niel *et al* [5, 6].

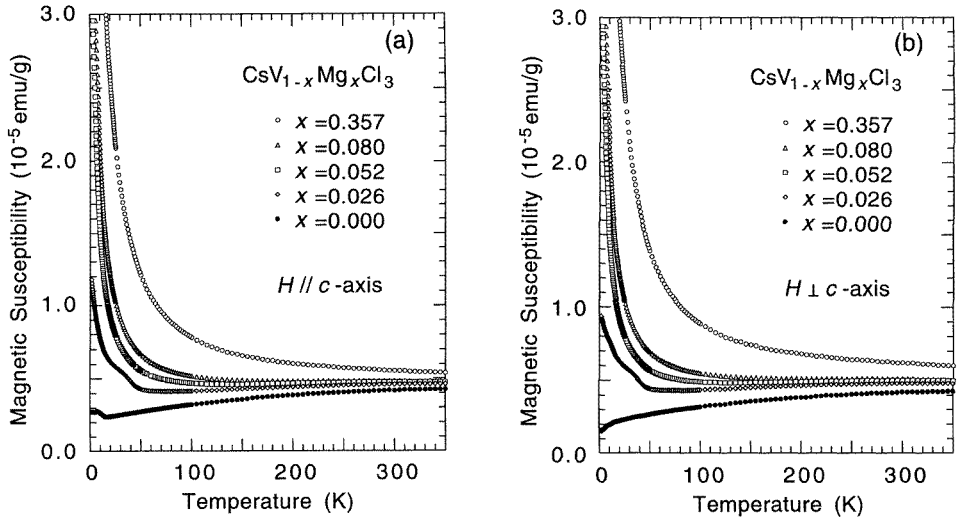

Figure 1. The temperature-dependence of the magnetic susceptibility for a field (100 Oe) applied parallel (a) and perpendicular (b) to the c axis.

3. Results

Figures 1(a) and (b) show the temperature-dependence of the magnetic susceptibility χ obtained for the field of 100 Oe applied parallel and perpendicular to the c axis. The susceptibility was converted into a value per gram of $CsVCl_3$ included in $CsV_{1-x}Mg_xCl_3$. We see a systematic change in susceptibility as x increases for both directions of applied field. The shoulder observed at about 35 K for $x = 0.026$ may be attributed to a 3D long-range ordering whose ordering temperature became higher than that of pure $CsVCl_3$ because

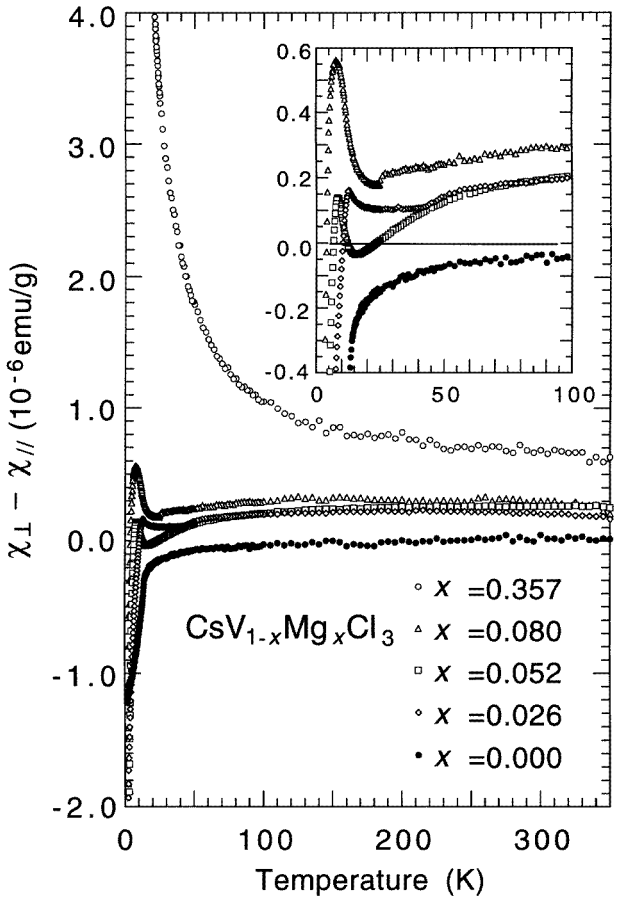

Figure 2. The temperature-dependence of $\chi_\perp - \chi_\parallel$. The inset shows a change of sign in $\chi_\perp - \chi_\parallel$ at low temperatures.

of a reduction in frustration. It is expected that the frustration of the spin arrangement in the basal triangular lattice plane is reduced because the number of magnetic ions is decreased.

In order to elucidate the anisotropy of χ, the value of $\chi_\perp - \chi_\parallel$ is plotted in figure 2, in which $\chi_\perp$ and $\chi_\parallel$ are the susceptibilities measured with a field perpendicular and parallel to the c axis. At all temperatures, the sample with $x = 0.357$ shows $\chi_\perp > \chi_\parallel$, whereas pure $CsVCl_3$ ($x = 0.000$) shows $\chi_\perp \leqslant \chi_\parallel$. A similar difference in anisotropy between pure and impure chains has been reported for TMMC doped with non-magnetic impurities of Cd and has been explained by the dipole coupling between magnetic ions within the segments of finite chain [4]. For $x = 0.026$, 0.052 and 0.080, $\chi_\perp - \chi_\parallel$ changes its sign in the low-temperature region below about 30 K. These samples also show a complicated behaviour, as we can see in the inset of figure 2. To investigate the paramagnetic behaviour of the finite chains, the susceptibility of pure $CsVCl_3$ ($x = 0.000$) was subtracted from that of impure samples. For $x = 0.052$, 0.080 and 0.357, the susceptibilities after the subtraction closely obey the Curie–Weiss law $\chi = C/(T - \Theta)$. The Curie constant C (emu K g^{-1}) and the Weiss temperature Θ (K) are listed in table 1. We see that the finite chains behave like paramagnetic spins with a weak antiferromagnetic interaction between them.

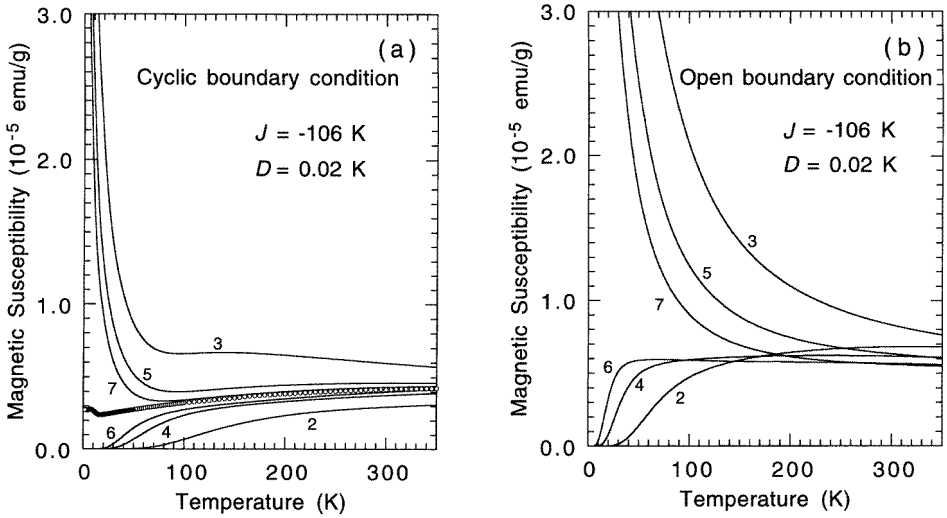

Figure 3. The magnetic susceptibility calculated for $S = \frac{3}{2}$ Heisenberg antiferromagnetic chains with up to seven spins with the cyclic (a) and the open (b) boundary conditions. The open circles are the experimental results for pure $CsVCl_3$ ($x = 0.000$) for H parallel to the c axis.

Table 1. A summary of the Curie constant and the Weiss temperature.

	H parallel to the c axis		H perpendicular to the c axis	
x	C (10^{-4} emu K g^{-1})	Θ (K)	C (10^{-4} emu K g^{-1})	Θ (K)
0.357	4.761 ± 0.006	-1.206 ± 0.005	5.710 ± 0.006	-1.052 ± 0.004
0.080	2.055 ± 0.004	-1.628 ± 0.008	2.252 ± 0.006	-2.051 ± 0.013
0.052	1.500 ± 0.003	-2.205 ± 0.011	1.655 ± 0.013	-2.909 ± 0.047

4. Discussion

Figures 3(a) and (b) show the magnetic susceptibility calculated for the $S = \frac{3}{2}$ HAF chain up to seven spins with the cyclic (a) and the open (b) boundary conditions using a parallel computer (Fujitsu VPP500/28) installed at RIKEN. That the calculation was performed only for $n \leqslant 7$, where n is the number of spins in a chain, is due to the limit of the computer memory. We used the Hamiltonian

$$\mathcal{H} = -2J \sum (S_i{}^x S_{i+1}{}^x + S_i{}^y S_{i+1}{}^y + S_i{}^z S_{i+1}{}^z) + D \sum (S_i{}^z)^2 - g\mu_B H \sum S_i{}^z \qquad (1)$$

where the first term corresponds to the exchange energy, the second to the single-ion anisotropy and the third to the Zeeman energy in which we set $g = 1.98$ [10]. The Hamiltonian was block-diagonalized according to its rotational symmetry. Whole eigenvalues and eigenstates including excited states were evaluated numerically by the exact-diagonalization of each block. Thermodynamic quantities were directly calculated from partition sums and correlation functions. All the calculation results were checked with the use of numerical differentiation.

As the value of D, we used 0.02 K evaluated from inelastic neutron scattering [11]. As we see in figures 3(a) and (b), the susceptibility calculated with the cyclic boundary condition converges faster than does that with the open boundary condition as n increases.

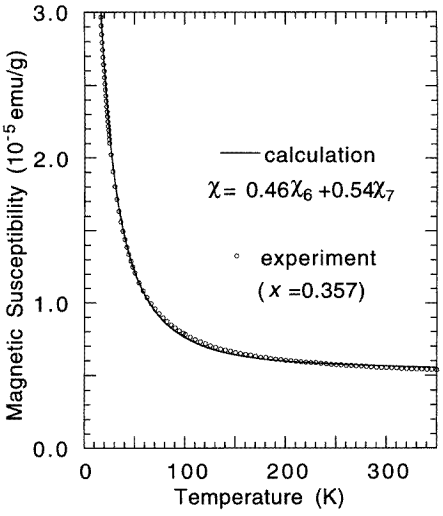

Figure 4. A weighted sum of the calculated susceptibilities and the experimental result of $x = 0.357$ for H parallel to the c axis.

We expect a curve for $n = \infty$ between the curves for $n = 6$ and 7 calculated with the cyclic boundary condition. From the fit of the theoretical curves to the experimental result for pure $CsVCl_3$ which corresponds to $n = \infty$, we get the value $J = -106$ K, whose absolute value is a little bit smaller than the value -115 K obtained before [5, 6].

Assuming that the magnetic interaction between the finite chains of V^{2+} ions is interrupted by the Mg^{2+} ions completely, the susceptibility obtained experimentally can be reproduced by a weighted sum of the susceptibility curves calculated with the open boundary condition taking the distribution of chain length into account. Let us try to reproduce the experimental result for $x = 0.357$. For the $x < 0.357$ samples, it is impossible to obtain a good fit to the susceptibility data because in these samples we expect the chain length to exceed seven sites. When we consider a case in which the 1D sites are occupied at random by V^{2+} and Mg^{2+} ions, the total number of V^{2+} ions which constitute the finite chains with n sites has a distribution peaked at $n = 2$ for $x = 0.357$. A weighted sum of the susceptibilities using the distribution based on random occupation, however, gives a much larger susceptibility than the experimental result for $x = 0.357$. This suggests that the distribution of chain length shifts to longer length because of a tendency for Mg^{2+} or V^{2+} ions to form clusters in 1D sites. Figure 4 shows the weighted sum $\chi = 0.46\chi_6 + 0.54\chi_7$, where χ_6 and χ_7 are the susceptibilities calculated for six and seven spins with the open boundary condition, and the susceptibility obtained for $x = 0.357$ for a parallel field. Since we have no information on the distribution of chain length, this weighted sum is one of the possibilities to reproduce the experimental result. The weighted sum $\chi = 0.46\chi_6 + 0.54\chi_7 = (0.46/6)6\chi_6 + (0.54/7)7\chi_7$ suggests that the finite chains with six and seven spins are almost the same in number ($0.46/6 \cong 0.54/7$). In this case, the average chain length of V^{2+} ions is 6.50 and the average length of Mg^{2+} ion cluster is approximately estimated to be $0.357/(1/6.50) = 2.32$. For the average length of 6.50, the total number of finite chains of V^{2+} ions is given by $N_A/6.50$ for 1 molar V^{2+} ions, where N_A is Avogadro's number. At low temperatures, we expect that the chains with an even number of ions have no net magnetic moment, whereas those with an odd number of ions

have a magnetic moment of $3g\mu_B/2$ per chain. Then we have the Curie constant

$$C \text{ (emu K g}^{-1}) = \chi T = \frac{(N_A/6.50)}{2}\frac{1}{m_M}\frac{{\mu_B}^2 g^2 S(S+1)}{3k_B} \tag{2}$$

where m_M is the molecular weight of $CsVCl_3$. From this expression, using the Curie constant 4.761×10^{-4} (emu K g^{-1}) given in table 1 for $x = 0.357$, the effective spin S_{eff} is estimated to be $S_{eff} = 1.49$, which is close to $\frac{3}{2}$. In the simplified treatment mentioned above, the spin reduction in the finite chain originating from a quantum effect is not confirmed. In estimating S_{eff}, it is essential to evaluate the total number of finite chains accurately from the distribution of chain length. The distribution may be directly observed using a magnetic force microscope.

5. Conclusion

In order to elucidate a finite-size effect in the $S = \frac{3}{2}$ 1D Heisenberg antiferromagnet, the temperature-dependence of the magnetic susceptibility of $CsV_{1-x}Mg_xCl_3$ ($x = 0.000$–0.357) was investigated. For $x \geqslant 0.052$, the susceptibility of the finite chains behaves like that of paramagnetic spins obeying the Curie–Weiss law. A change of sign in $\chi_\perp - \chi_\parallel$ was observed below about 30 K for $0.026 \leqslant x \leqslant 0.080$. From the comparison between the experimental results and the results of the exact-diagonalization method for chains with up to seven spins, the intrachain exchange coupling constant was estimated to be $J = -106$ K. The experimental result for $x = 0.357$ was reproduced by a weighted sum of the susceptibilities calculated with the open boundary condition. It is suggested that Mg^{2+} ions have a tendency to form clusters at the 1D sites.

Acknowledgment

One of us (HY) acknowledges the support of the Special Postdoctoral Researchers Programme from RIKEN.

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