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Regular versus alternating $(FeS_4)_n$ chains: Magnetism in $KFeS_2$ and $CsFeS_2$

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We report crystal magnetic susceptibility results of two $S=1/2$ one-dimensional Heisenberg antiferromagnets, $KFeS_2$ and $CsFeS_2$. Both compounds consist of $(FeS_4)_n$ chains with an average Fe-Fe distance of 2.7 Å. In $KFeS_2$, all intrachain Fe-Fe distances are identical. Its magnetic susceptibility is typical of a regular antiferromagnetic chain with spin-spin exchange parameter $J=-440.7$ K. In $CsFeS_2$, however, the Fe-Fe distances alternate between 2.61 and 2.82 Å. This is reflected in its magnetic susceptibility, which could be fitted with $J=-640$ K, and the degree of alternation, $\alpha=0.3$. These compounds form a unique pair, and allow for a convenient experimental comparison of the magnetic properties of regular versus alternating Heisenberg chains. [S0163-1829(97)07737-0]

I. INTRODUCTION

We report the single-crystal magnetic susceptibility of two $S=1/2$ one-dimensional magnetic systems, $KFeS_2$ and $CsFeS_2$. These compounds form a rather unique pair. Both consist of $(FeS_4)_n$ chains, formed by edge-sharing FeS_4 tetrahedra, with an average Fe-Fe distance of 2.7 Å.[1] In the potassium compound, all Fe-Fe distances are identical, but in the cesium compound it alternates between 2.61 and 2.82 Å.[1] These compounds, therefore, allow for a convenient experimental comparison of the magnetic properties of regular vs alternating Heisenberg $S=1/2$ chains.

The study of one-dimensional quantum magnets is of great current interest because of the rich phase diagrams and a variety of phenomena associated with these systems.[2] One-dimensional $S=1/2$ systems are particularly appealing since their properties are likely to be dominated by quantum effects. Alternating linear chains have aroused interest for their relation to organic free radicals and spin-exciton theory and in connection with the spin-Peierls theory.[3] There has been a continuing search for new linear $S=1/2$ systems which could verify existing models, and are capable of exhibiting interesting phenomena. Homologous families, in particular, are attractive since the effect of the degree of alternation on the magnetic phenomena may easily be demonstrated. Exchange-coupled transition-metal compounds with alternatingly spaced *linear* structures are rare. One of the most widely studied systems, $Cu(NO_3)_2$, has, in fact, a ladderlike structure at room temperature.[4] The more recently studied $(VO)_2P_2O_7$, too, has the V^{4+} $(S=1/2)$ ions in a ladderlike configuration.[5] Almost all of the previously reported alternating linear chain systems are Cu based.

The crystal structure of $KFeS_2$ $(C2/c)$ and $CsFeS_2$ (I_{mmm}), are similar with four molecules per unit cell. The Fe atoms in both the structures are coordinated tetrahedrally to four sulfur atoms. The FeS_4 tetrahedra are linked together by edge sharing to form chains which run parallel to the c axis of the crystal. In both $KFeS_2$ and $CsFeS_2$, the Fe atoms lie on the chain, but while in the former they are equally spaced at 2.7 Å, in the latter the Fe-Fe distances alternate between 2.61 and 2.82 Å (Fig. 1). In both compounds, the interchain Fe-Fe distance is 7 Å, and consequently, both $KFeS_2$ and $CsFeS_2$ have a pronounced one-dimensional character. The Fe-S distances in both compounds are remarkably short (~2.2 Å), leading to strong ligand fields with Fe atoms in the low-spin $S=1/2$ state.[1] The FeS_4 tetrahedra are distorted with Fe-S distances varying between 2.18 and 2.28 Å. This reduction in symmetry leads to a quenching of the orbital angular momenta, and consequently, the exchange interactions are isotropic.

$CsFeS_2$ undergoes a first-order structural and magnetic phase transition at 70 K.[6] The transition is martensitic in character with considerable hysteresis, and consequently, the magnetic data for temperatures lower than ~100 K have not been presented here. $KFeS_2$ undergoes a Néel transition to a three dimensionally ordered antiferromagnetic state at 250 K.[7] It has recently been established that the high-temperature magnetic behavior of $KFeS_2$ is typical of a spin-1/2 Heisenberg chain.[8] Similar considerations would make $CsFeS_2$ a spin-1/2 alternating Heisenberg chain, or a spin-Peierls ground-state system, and that is the focus of the present study. In these systems, anisotropic susceptibility studies are necessary to establish whether the system has a true spin-Peierls ground state, or whether it is in a dimerized Néel state.

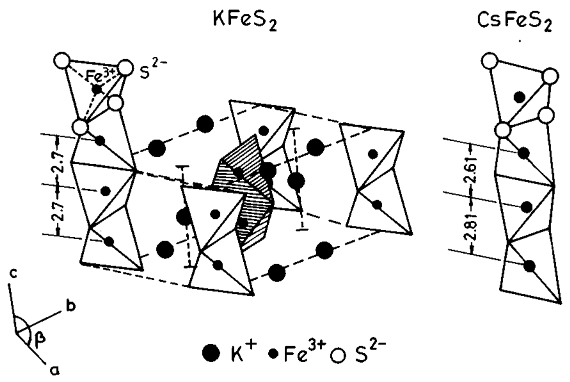

FIG. 1. The structure of $AFeS_2$ (A=K, Cs), (a) the uniform chain $KFeS_2$, and (b) the structure of the dimerized $(FeS_4)_n$ chains in $CsFeS_2$.

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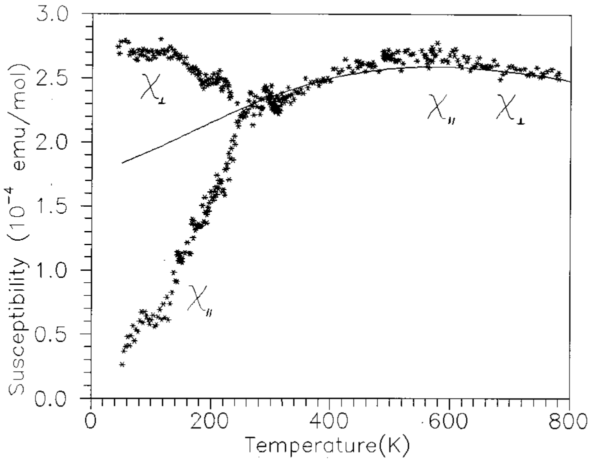

FIG. 2. The experimental crystal magnetic susceptibility of $KFeS_2$, with the external field applied parallel and perpendicular to the c axis. The solid line is the calculated Bonner-Fisher susceptibility for a uniform chain with $J=-440.71$ K.

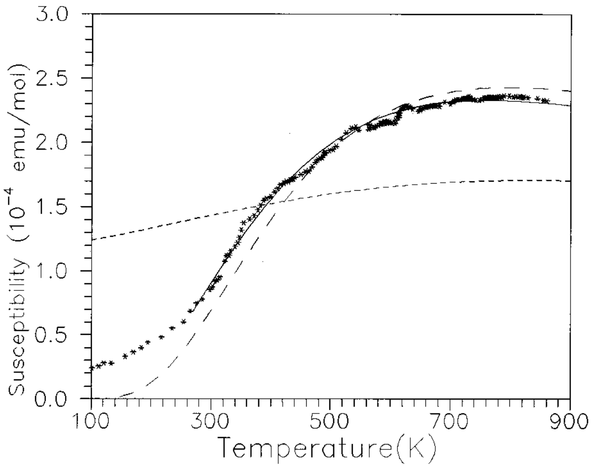

FIG. 3. Experimental crystal magnetic susceptibility of $CsFeS_2$, with the external field applied parallel and perpendicular to the c axis. The solid line is the susceptibility of a dimerized chain with $J=-640$ K, and $\alpha=0.3$. The dashed lines are the calculated susceptibilities for a uniform chain and for an isolated dimer for the same value of J.

II. EXPERIMENT

The alkali metal thioferrates, $KFeS_2$ and $CsFeS_2$, were prepared by heating a 4:1 mixture of the anhydrous alkali metal carbonate and oxide-free iron powder in a stream of dry H_2S at 1000 K for 24 h. The product was cooled to ambient temperatures over a period of 24 h, and then extracted with cold water. Permanganate colored needlelike crystals, typically 5–10 mm in length and ~ 1 mm wide, were obtained. The crystals were again heated in flowing H_2S at 773 K for 12 h. This is an important step since, under these conditions, surface oxide impurities, formed during the extraction, are converted back to sulfides. The oxides being ferromagnetic, can mask the true susceptibility of the sulfides, which are small. Magnetic susceptibility measurements were made on a Faraday magnetic balance. A large number of needlelike crystals were aligned parallel onto a thin quartz plate using silicone grease. The plate was then suspended from the balance by an arrangement similar to that reported in Ref. 9. For high-temperature measurements, the crystals were tightly packed with the needle axis aligned parallel to each other and sealed under vacuum in small thin walled quartz ampoules. Calibration with $HgCo(NCS)_4$ was repeated under similar conditions. The susceptibilities reported are for two directions; applied field parallel and perpendicular to the c axis, which is also the needle axis of the crystals. The diamagnetic as well as van Vleck temperature-independent paramagnetic contributions have been subtracted.

III. RESULTS AND DISCUSSION

The magnetic susceptibility of $KFeS_2$ and $CsFeS_2$ with the applied field parallel ($\chi_\parallel$), and perpendicular ($\chi_\perp$), to the chain axis is shown in Figs. 2 and 3, respectively. The susceptibility of $KFeS_2$ (Fig. 2) is typical of an one-dimensional magnetic system undergoing a three-dimensional antiferromagnetic ordering at 250 K. Above 250 K, the susceptibility is isotropic, and shows a broad maximum at 565 K ($\chi_{\max}=2.7\times10^{-4}$ emu/mol). The value of the quantity $\chi_{\max}T_{\max}/g^2$, which is characteristic of the spin state of the linear chain, is 0.375, typical of a $S=1/2$ chain.[10] [In $KFeS_2$, the EPR determined value of g is 2.025 (Ref. 11).] In contrast, the magnetic susceptibility of $CsFeS_2$ (Fig. 3) is isotropic over the entire temperature range studied, and shows a broad maximum at 800 K ($\chi_{\max}=2.35\times10^{4}$ emu/mol).

The Hamiltonian for a linear chain may be written as

$$\mathcal{H}=-2J\sum_{i=1}^{N/2}(S_{2i-1}S_{2i}+\alpha S_{2i}S_{2i+1}) \tag{1}$$

where J is the exchange parameter between the ith spin and its $(i-1)$th neighbor. $\alpha=J_1/J$ is the degree of alternation. J_1 is the exchange constant between the ith and $(i+1)$th spin. When $\alpha=1$, the uniform Heisenberg chain is obtained, and when $\alpha=0$, the system breaks up into noninteracting dimers.

For a uniform chain, the maximum in susceptibility is uniquely defined by the Bonner-Fisher relation[12]

$$\frac{k_B T_{\max}}{-J}=1.282, \tag{2}$$

where k_B is the Boltzmann constant. For $KFeS_2$, this leads to a value of $J=-440.7$ K. The three-dimensional antiferromagnetic transition implies the existence of appreciable interchain exchange, J'. This may be evaluated from the relationship between T_N and J/J' derived by Oguchi.[13] The value of J', so obtained, is 53.9 K.

For an alternating chain no such unique relationship exists. We have used a prescription given by Bonner *et al.*,[14] who showed that for an alternating chain,

$$\frac{k_B T_{\max}}{-J}\approx 1.25 \tag{3}$$

and is independent of α. This gives an approximate value of $J=-640$ K for $CsFeS_2$.

We have calculated the susceptibility over the entire temperature range from the theoretical susceptibility curves for linear and alternating Heisenberg antiferromagnetic chains using parametrizations due to Torrance *et al.*[15] for the regular chain, and Hatfield[16] for the alternating chain. For $KFeS_2$, the susceptibility was calculated for a linear chain with $J = -440.7$ K. The interchain interactions were treated in the mean-field approximation using $J' = 53.9$ K by the following relation:

$$\chi = \frac{\chi_{\mathrm{chain}}}{[1-(2zj'/Ng^2\mu_B^2)\chi_{\mathrm{chain}}]}. \tag{4}$$

The calculated susceptibility is shown as the solid line in Fig. 2.

The parametrized theoretical susceptibility of an alternating chain[16] was fitted to the experimental susceptibility of $CsFeS_2$ allowing J and α to float. The best fit was obtained for $J = -640$ K and $\alpha = 0.3$, and is shown as the solid line in Fig. 3. The dashed lines in Fig. 3 are the calculated magnetic susceptibility of an isolated $S = 1/2$ dimer $(\alpha = 0)$, and of a regular linear chain, with $J = -640$ K $(\alpha = 1)$.

The results of Fig. 3 show that $CsFeS_2$ provides a striking example of a $S = 1/2$ alternating Heisenberg chain. As compared to most of the Cu^{2+} compounds which exhibit alternating behavior,[17] in $CsFeS_2$, the alternating behavior is manifest at much higher temperatures because of the greater value of J. It is interesting to note that the exchange constant in $KFeS_2$ (Fe-Fe = 2.7 Å), -440.7 K, is close to the mean of $J = -640$ K (Fe-Fe = 2.61 Å) and $J_1 = 192$ K (Fe-Fe = 2.82 Å) found in $CsFeS_2$.

It is interesting to compare the magnetism in $KFeS_2$ and $CsFeS_2$ with that of a spin-Peierls system. A spin-Peierls system is, of course, different—it behaves as an assembly of uniform chains above a transition temperature, and below this temperature, progressive spin-lattice dimerization effectively gives rise to an assembly of alternating chains. $KFeS_2$ and $CsFeS_2$ may be considered as the high-temperature and low-temperature analogs of a hypothetical spin-Pierls system in which the distance between the spins is 2.7 Å above the transition temperature, and below the temperature alternates between 2.61 and 2.81 Å.

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