Spin-lattice instability in the chromium sulfur spinel $Fe_{0.5}Cu_{0.5}Cr_2S_4$

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Abstract

Zero field μSR spectroscopy was applied to a polycrystalline sample of the ferrimagnetic sulfur spinel $Fe_{0.5}Cu_{0.5}Cr_2S_4$ between 5 and 315 K. The temperature dependence of the interstitial magnetic field B_μ as well as the transverse and longitudinal relaxation rates were deduced. At around 100 K, the temperature dependence of the interstitial field exhibits a strong deviation from the expected Brillouin-like behavior together with a maximum of the transverse relaxation rate. These features are characteristic for a spin reorientation transition. This instability of the ferrimagnetic spin-lattice has not been reported previously. ^{57}Fe Mössbauer data from the same sample show no irregularity in the temperature dependence of the Fe hyperfine field which could indicate that the spin reorientation involves primarily the Cr sublattice. Above and below the spin reorientation regime, disorder in the spin-lattice is sizable, but not excessive. At low temperatures, the spins are essentially static, spin dynamics sets in above the reorientation range. The μSR data are also complemented by new susceptibility and magnetization data taken on similar material.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

During the last decade spinels and, in particular, chromium based spinels have attracted considerable attention: the occurrence of colossal magnetoresistance (CMR) [1, 2], experimental evidence of multiferroicity [3–6] and detailed studies of strong spin-phonon coupling effects [7–10] have been reported. In the normal spinel structure with stoichiometry AB_2X_4, the A ions are tetrahedrally coordinated, while the B ions exhibit an octahedral coordination by X ions, which can be either oxygen, sulfur or selenium [11]. One distinguishes between A site and B site magnetic spinels, depending on the location of the magnetic ion. Both sites reveal strong frustration effects; magnetic moments located on the diamond lattice built up by the A site ions reveal complex ground states [12–15], which critically depend on the ratio of the nearest neighbor and next-nearest neighbor exchange [15]. The B sites span a network of corner sharing tetrahedra, the well-known pyrochlore lattice, which is one of the most strongly frustrated three-dimensional lattices. In the chromium oxides, which are governed by direct antiferromagnetic exchange between neighboring chromium moments, conventional long-range spin order is suppressed and exotic ground states are established at low temperatures [16].

The system under consideration, copper doped $FeCr_2S_4$ can be termed an AB spinel since the magnetic ions occupy both the A and the B sites, respectively. For both

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sites the magnetic exchange is transmitted by indirect exchange and AB spinels usually reveal collinear ferrimagnetic structures [11]. $FeCr_2S_4$ is a ferrimagnetic semiconductor with a Curie temperature around 170 K. The Fe and Cr ions each form ferromagnetic sublattices which are coupled antiferromagnetically [17]. Recent low temperature specific heat measurements combined with dielectric spectroscopy gave evidence for freezing of orbital moments into a glassy phase around 10 K [18]. It is possible to substitute Fe in part by Cu creating the alloy series $Fe_{1-x}Cu_xCr_2S_4$. A detailed study of the electronic transport and bulk magnetic properties of this series has been published [2]. Within the range from $x = 0$ to 0.5 the spinel structure remains unaltered and the ferrimagnetic order is maintained [17]. With increasing Cu content the lattice constant decreases and T_C increases while the CMR effect is reduced. In $Fe_{0.5}Cu_{0.5}Cr_2S_4$, neutron powder diffraction revealed saturated ordered moments of 2.3 μ_B for Fe and 2.7 μ_B for Cr [19]. Interestingly, starting from a simple antiparallel spin arrangement of the Fe and Cr ions, the refinements of the magnetic structure could be improved by allowing a canting of Fe spins in the x–y plane and of Cr spins toward $-x$ [19]. Orbital freezing is absent [18].

^{57}Fe Mössbauer spectroscopy showed that the Fe valence state changes from 2+ at $x = 0$ to 3+ for $x = 0.5$ [19, 20]. At intermediate Cu concentrations the two valence states coexist in an inhomogeneous mixture. Being considered a simple collinear ferrimagnet, $Fe_{0.5}Cu_{0.5}Cr_2S_4$ had attracted particular interest as a model substance to probe the mechanism of the CMR behavior of chromium spinels [19, 21].

We performed a μSR study on $Fe_{0.5}Cu_{0.5}Cr_2S_4$ to gain information on possible local disorder in its long-range ordered spin-lattice and on low frequency spin fluctuations. μSR spectroscopy is a tool particularly well suited for that purpose. As will be demonstrated in this communication, our μSR study unexpectedly revealed that the magnetism of $Fe_{0.5}Cu_{0.5}Cr_2S_4$ is not quite as simple as thought. μSR clearly detected an instability in the ferrimagnetically ordered spin-lattice which has not been reported previously.

After the μSR work had been completed, we reinvestigated carefully the magnetic susceptibility of $Fe_{0.5}Cu_{0.5}Cr_2S_4$ in field cooling (FC) and zero field cooling (ZFC) runs, in order to look for corresponding anomalies also in the bulk magnetic properties.

2. Experimental details

The samples in the form of polycrystalline thin platelets were prepared by solid state reactions from high purity elements. Their quality was checked by x-ray diffraction. Single phase material with a lattice constant of $a = 9.9257$ Å was confirmed. To study the bulk magnetic properties, the magnetization of $Fe_{0.5}Cu_{0.5}Cr_2S_4$ has been measured using a SQUID magnetometer (MPMS, Quantum Design) for temperatures between 2 and 400 K.

The results of the magnetization measurements at low external fields ($\mu_0 H = 5$ mT) are shown in figure 1. From these measurements we determined a Curie temperature for the onset of ferrimagnetic order of $T_C = 347$ K in good

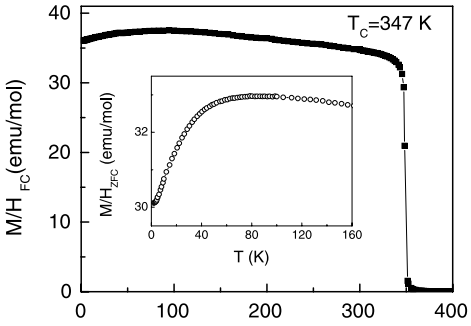

Figure 1. Field cooled magnetization of $Fe_{0.5}Cu_{0.5}Cr_2S_4$ in a weak external field of $\mu_0 H = 5$ mT. The inset shows the corresponding zero field cooled (ZFC) branch on an expanded scale.

agreement with previous published results [21]. At 4 K the saturated moment in the polycrystalline sample amounts to 3.2 μ_B per $Fe_{0.5}Cu_{0.5}Cr_2S_4$ formula. In the compound under consideration the octahedrally coordinated chromium ions have a half filled t_{2g} triplet ground state with spin $S = 3/2$. Fe and Cu are located at the tetrahedral A sites. For $Fe_{0.5}Cu_{0.5}Cr_2S_4$, Mössbauer spectroscopy [20] revealed a 3+ valence state of Fe, corresponding to a half filled d-shell with $S = 5/2$. In a simple collinear structure—under the assumption of spin-only moments and neglecting all spin–orbit effects—we hence expect a net ferromagnetic moment of approximately 3.5 μ_B, in reasonable agreement with the experimentally observed value of 3.2 μ_B. Already the field cooled measurements revealed a slight anomaly in the magnetization at low temperatures. To study this behavior in more detail, we determined additionally the zero field cooled (ZFC) magnetization, which usually is more sensitive than FC measurements. The temperature dependence of the ZFC susceptibility reveals a maximum close to 100 K and a subsequent decrease toward lower temperatures, as documented in figure 1.

For the μSR measurements, the platelets were mounted between thin aluminized Mylar foils and positioned inside the center tube of a He-flow cryostat. Temperatures could be set between 2 and 315 K with temperature stability better than 0.1 K. The samples are located inside the He flow which ensures proper sample temperature. The μSR spectra were measured in zero applied field (ZF) at the Swiss Muon Source (PSI) employing the surface muon beam 'πM3' in conjunction with the GPS spectrometer. The 'veto' mode [22] was enabled which suppresses the background signal from muons stopped outside the sample in the sample holder or the cryostat walls.

In a μSR experiment, a beam of fully spin polarized muons impinges on the sample. The muon spins are oriented parallel to the beam direction. In a time short compared to their mean life (2.2 μs), the muons come to rest at an interstitial lattice site (*a priori* not known) maintaining their spin polarization. When decaying, the muon emits a positron preferentially in the direction of its spin. This creates an asymmetry in the count rates of two positron detectors located along the beam direction forward and backward with respect to the sample position.

The muon spin will perform Larmor precession if a magnetic field B_μ is present at the muon stopping site. The spin motion causes a time modulation of the backward–forward count rate asymmetry $A(t)$ which is usually described by:

$$A(t) = A_0 G(t). \quad (1)$$

Here, A_0 is the initial ($t = 0$) asymmetry, typically around 0.2, depending in detail on the geometrical conditions of the μSR spectrometer. $G(t)$ is the muon response function describing the time evolution of polarization of the ensemble of implanted muons. Its form depends on the magnetic properties of the sample material. A plot of $A(t)$ versus t represents the μSR spectrum. The spectral data are usually least squares fitted to a function $G(t)$. Its parameters are the quantities of interest.

The interstitial magnetic field B_μ can have its origin in an applied field or in the magnetic dipole moments (either electronic or nuclear) of the atoms surrounding the stopped muon. Our measurements were carried out in zero applied field and we are concerned with the static and dynamic properties of the field inside the sample generated by the electronic moments of the magnetic ions (Fe and Cr).

More details on the μSR technique can be found, for example, in [23–27].

3. Results

The Mössbauer measurements [20], gave a Curie temperature of ∼340 K for polycrystalline $Fe_{0.5}Cu_{0.5}Cr_2S_4$, in good agreement with our susceptibility data. Other magnetic studies listed similar values for T_C. Hence we can expect that, over the whole temperature range covered, our sample exhibits long-range ferrimagnetic order. In a long-range magnetically ordered material the muon response function for a powder sample takes the form:

$$G(t) = \tfrac{2}{3}\cos(\nu_\mu t + \Phi)\exp(-\lambda_{trans} t) + \tfrac{1}{3}\exp(-\lambda_{long} t) \quad (2)$$

with $\nu_\mu = (\gamma_\mu/2\pi)B_\mu$, the muon precession frequency, and $\gamma_\mu/2\pi = 135.5$ MHz/T, the muon gyromagnetic factor. Φ is a phase factor, usually close to zero in a backward–forward measuring geometry. Equation (2) reflects the assumption that the internal field vector is parallel to each of the three Cartesian directions with equal probability. Taking one axis as the direction of the initial muon spin, then in 1/3 of the cases the field is oriented parallel to the muon spin and thus will not exhibit Larmor precession. Fluctuations of the electronic spins (and with them of the internal field) relax the muon spin polarization which is described by the second term of equation (2). The longitudinal relaxation rate λ_{long} is a measure of electronic spin fluctuations. In the static limit one has $\lambda_{long} = 0$. With increasing fluctuation rate λ_{long} increases. The longitudinal rate is the equivalent of $1/T_1$ in NMR [28]. In 2/3 of the cases the internal field is oriented perpendicular to the muon spin and causes muon spin precession with frequency ν_μ described by the cosine factor in the first term of equation (2). A distribution of the local field around its mean value results in a distribution of precession frequencies causing a damping of the oscillatory pattern. The exact form of the damping factor depends on the form of the field distribution. By experience, the situation is usually well enough described by exponential damping, as given in the first term of equation (2). The transversal relaxation rate is a measure of the field distribution width, it increases with increasing width. One can view λ_{trans} as the equivalent of $1/T_2$ in NMR. Strictly speaking λ_{trans} contains also a contribution from field fluctuation, but in general this can be neglected.

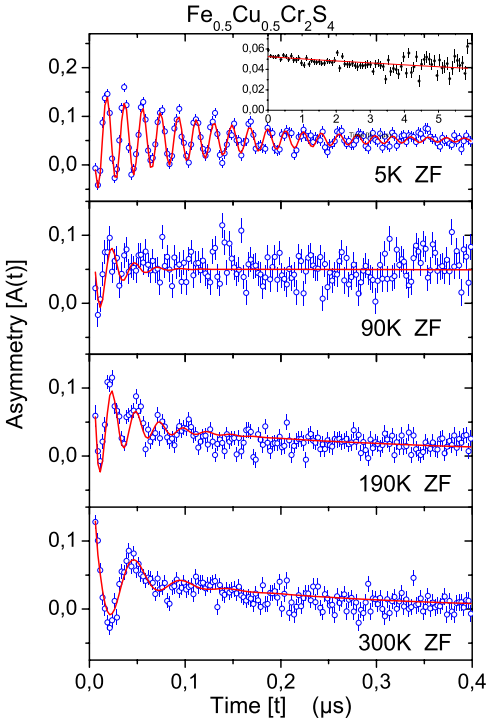

Figure 2. Zero field μSR spectra of $Fe_{0.5}Cu_{0.5}Cr_2S_4$ at selected temperatures. Shown is the initial part of the spectra, except for the 5 K case where the insert shows the full spectrum in low resolution. The solid lines are least squares fits to the function $G(t)$ of equation (2). Details are given in the text.

The ZF μSR measurements on $Fe_{0.5}Cu_{0.5}Cr_2S_4$, carried out between 5 and 315 K, all resulted in spectra which can well be described by the formalism of equation (2). Some of those spectra at selected temperatures are depicted in figure 2. The muon spin precession pattern is clearly visible in the early times part of the spectrum under high time resolution (2.5 ns/bin). The damping of the oscillations is fairly strong, meaning that λ_{trans} is sizable. Also shown as an inset in the 5 K panel is the full spectral time range plotted in low time resolution (60 ns/bin). The low resolution averages out the oscillations at early times and the plot thus depicts the time dependence of the longitudinal spectral term (1/3 signal). The plot demonstrates that λ_{long} must be rather small since the decay of asymmetry is very slow. Even within the full time range the spectral baseline ($A(t) \equiv 0$) is not reached. The most pronounced change in the 90 K spectrum is the dramatic increase of λ_{trans} which damps out the oscillatory pattern very quickly. At higher temperatures (e.g. 190 K), the damping gets smaller again and the oscillations become once more better visible. Also at higher temperatures (190 and 300 K in figure 2) one finds the spectral baseline to be reached essentially within

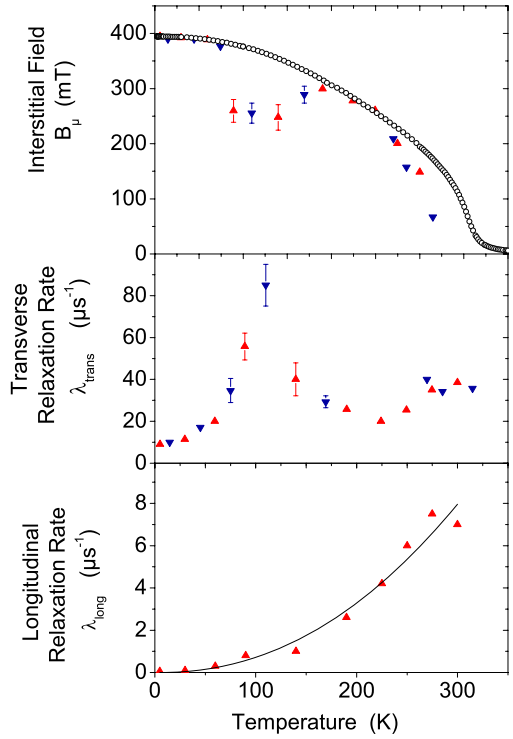

Figure 3. Temperature dependences of the parameters B_μ, λ_{trans} and λ_{long} as derived from fitting $G(t)$ of equation (2) to the measured spectra. The open circles in the top panel are the experimental magnetization curve measured in an external field of 1 T normalized to the μSR data in the low temperature limit. The results from two sets of μSR data are depicted. The difference between set 1 (up-triangle) and set 2 (down-triangle) is explained in text. For set 2 we have concentrated on the oscillatory signal, thus λ_{long} was not evaluated. The solid line shows the power law fit discussed in the text. The error on the data points is smaller than the size of the plot symbols, except where error bars are given.

the span depicted in the early times plot, meaning that now λ_{long} has markedly increased.

The temperature dependences of the physically relevant parameters B_μ (as derived from ν_μ), λ_{trans}, and λ_{long} are presented in figure 3. The results of two sets of measurements are shown. Set 1 was carried out with a large powder sample. Set 2 refers to data obtained from a small part of the material used in set 1. This small sample is the one used in the Mössbauer measurements to be discussed in the next section. This was done to ensure that the μSR and Mössbauer results can safely be compared. The fact that the results of the two runs are quite comparable also demonstrates the magnetic uniformity of the sample material used.

4. Discussion

In $Fe_{0.5}Cu_{0.5}Cr_2S_4$ both ferromagnetic sublattices enter long-range order at the same second order critical temperature ($T_C \approx$ 340 K) [17, 18]. Under these circumstances, the magnitude of the mean magnetic field B_μ at the muon site should follow closely the magnetization curve. Yet, as can be discerned from the top panel of figure 3, this is not the case. Coming from the low temperature side, the temperature dependence of B_μ begins to fall well below the magnetization curve around 90 K and remains there up to approximately 190 K. At this temperature the value of B_μ again comes close to those of the magnetization curve but on approaching the phase transition the internal field falls off more sharply than the magnetization.

Concurrently with the reduction of B_μ, the transverse relaxation rate rises sharply, peaking near 110 K, and then decreases rapidly with rising temperature (center panel of figure 3). Such features are the characteristic μSR response around a spin reorientation transition.

The case most thoroughly studied by μSR is the spin reorientation in ferromagnetic gadolinium metal [23, 29, 30]. The crystal structure of Gd is hcp. Below $T_C = 293$ K, the Gd^{3+} moments point along the c-axis. In the temperature region between 245 and 220 K the moments turn away from the c-axis, finally reaching a tilt angle of about 60°. This turning of electronic spins is reflected in a lowering of B_μ compared to the values expected from the magnetization curve. Here, as well, one observes a distinct peaking of the transverse relaxation rate in the spin reorientation range. Overall the data on Gd are quite analogous to those seen in $Fe_{0.5}Cu_{0.5}Cr_2S_4$ (e.g. when comparing figures 1 and 3 of [29] with figure 3 top and center panels).

The magnetic field B_μ at the muon site is, especially in poor conductors, mainly generated by the dipolar fields of the electronic spins surrounding the stopped muon. Dipolar fields are highly anisotropic, hence turning the electronic spins will result in a strong change of B_μ. For this reason μSR spectroscopy is a particularly sensitive tool for exploring the spin turning processes. A detailed treatment of the analysis of the μSR response at spin reorientations has been given by [31]. In the present case a quantitative analysis is not possible since the interstitial lattice site where the muon rests is not known.

The sharp rise in λ_{trans} within the spin reorientation regime signals that the magnetic moments do not turn uniformly within macroscopic volumes (e.g. the sample size). Rather a distribution of turning angles is present between the start and the end of the reorientation transition which leads to a distinct disorder in the spin-lattice reflected in the large value of λ_{trans}. This non-uniformity of spin turning was extracted in more detail in the Gd data [30] using a two component spectral fit. The stronger damping rate in the case of $Fe_{0.5}Cu_{0.5}Cr_2S_4$ rendered such an approach unreliable. The parameters of the two component fit were too highly correlated and depended strongly on the choice of the start parameters. Hence this approach was not further pursued. The longitudinal relaxation rate stays at low values over the reorientation regime. This means that B_μ, and with it the electronic spins, remain largely in the near static limit, hence the spin reorientation is not connected to specific spin fluctuations.

Another well-known case where the deviation of the temperature dependence of B_μ from that of the macroscopic magnetization signaled a spin rotation transition is the permanent magnet $Nd_2Fe_{14}B$ [32].

To our knowledge, the spin reorientation transition in $Fe_{0.5}Cu_{0.5}Cr_2S_4$ has escaped detection thus far. The only temperature dependence of the Fe and Cr magnetic moments derived from neutron diffraction can be found in [19].

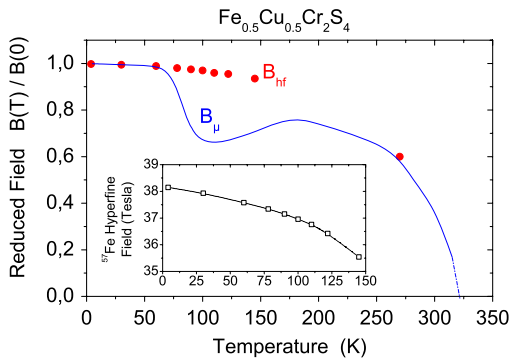

Figure 4. Comparison of the temperature dependences of the reduced hyperfine field from Mössbauer spectroscopy (filled circles) and the interstitial field from μSR spectroscopy (line). The inset shows the Mössbauer field data on an extended scale. The line through the data points is a guide to the eye. Error bars are negligible even on the extended scale.

Unfortunately, the next higher temperature point after the low temperature limit (∼4 K) is at 200 K, excluding the region where the spin turning occurs. Although only a few temperatures were measured, the data show that the temperature dependences of the Fe and Cr moments are alike and that a common magnetic transition point exists.

In the Mössbauer data reported previously [20, 33], the temperature dependence of the ^{57}Fe hyperfine field is smooth with no irregularity at temperatures around 100 K. To establish that this result also holds for our sample material we have recorded Mössbauer spectra with high accuracy in the temperature regime where the spin reorientation has been observed with μSR. Figure 4 shows our result. The main plot compares the temperature dependences of the reduced ^{57}Fe hyperfine field and interstitial field B_μ. The inset shows the variation of the hyperfine field on an extended scale. Clearly no irregularity is present at all. As mentioned above, we have repeated the μSR spectroscopy using the Mössbauer sample (set 2 in figure 3). The result confirms that the two measurements can safely be compared and that indeed the ^{57}Fe hyperfine field in $Fe_{0.5}Cu_{0.5}Cr_2S_4$ is not at all disturbed by the spin reorientation process. It was further confirmed that all Fe ions are in the 3+ valence state.

One may argue that the hyperfine field at the nucleus of the magnetic ion is dominantly sensitive to the electronic configuration of the atomic shell producing the magnetic moment, but is not very sensitive to the orientation of this moment with respect to the crystalline axes. Probably the most thorough Mössbauer study of spin reorientation is the Morin transition in α-Fe_2O_3 (hematite) [34]. At the Morin transition, located at 264 K (i.e. well below $T_C = 955$ K), the magnetic structure changes from simple antiferromagnetism to weak ferromagnetism due to spin canting. The transition is faintly visible as a reduction of about 2% in the magnitude of the hyperfine field. In contrast, a μSR study of the Morin transition [35] gave a change in B_μ of about 50%, emphasizing the already mentioned high sensitivity of μSR to spin reorientation phenomena. The manifestation of the spin reorientation in α-Fe_2O_3 by Mössbauer spectroscopy is helped by the fact that the local surrounding of Fe is noncubic and a distinct quadrupolar interaction is present in the hyperfine spectra. At the Morin transition the change in quadrupolar interaction is quite substantial (actually a change in sign occurs). Such additional information is not available here since the local symmetry of the Fe ion in $Fe_{0.5}Cu_{0.5}Cr_2S_4$ is cubic.

Independently of these considerations, the Mössbauer results on $Fe_{0.5}Cu_{0.5}Cr_2S_4$ show that a change in electronic structure affecting the magnitude of the magnetic moment is absent, at least for the Fe sublattice. Our data put the limit of a possible change in the magnitude of the hyperfine field to about 0.3%. This may indicate that the major effect of spin reorientation occurs in the Cr sublattice and that the Fe sublattice is much less involved. It is, however, unreasonable to assume that the Cr lattice alone suffers from spin turning and that the Fe lattice is totally decoupled from this occurrence.

Excluding the spin reorientation region, the μSR response of $Fe_{0.5}Cu_{0.5}Cr_2S_4$ is what one expects from a long-range ordered magnet. The transverse relaxation rate at low temperatures is sizable but not excessive. Its somewhat enhanced value probably arises from disorder on the A site due to its random occupation by Fe and Cu ions. Spin dynamics, as reflected in the magnitude of λ_{long}, increases toward T_C, which is typical for a second order transition. It has been pointed out [36] that in a ferromagnetic spin structure, the muon spin relaxation occurs via a Raman scattering process involving two magnons. Under the condition of a Heisenberg ferromagnet the longitudinal relaxation rate takes the form of a power law:

$$\lambda_{long}(T) = CT^2 \ln T. \qquad (3)$$

The constant C contains the magnon stiffness. The rare earth intermetallic $GdNi_5$ provided a fine experimental observation of this predicted behavior, leading to a magnon stiffness constant in the proper range [37]. A fit according to equation (3) to $\lambda_{long}(T)$ of $Fe_{0.5}Cu_{0.5}Cr_2S_4$ worked quite satisfactorily as demonstrated in the lower panel of figure 3. This establishes that the mechanism of muon spin relaxation as reflected in λ_{long} is the two magnon Raman process as in a simple ferromagnetic spin-lattice. The theoretical details leading to the expression of equation (3) are fairly complex. The connection to the magnon stiffness constant contains a geometrical factor G depending on the local symmetry of the muon stopping site [38]. This information is at present lacking here. Hence we have not proceeded to a quantitative analysis, but remark that the relaxation rate, especially closer to the Curie temperature, is comparatively large, a probable outcome of magnetic frustration.

The magnetization data presented in figure 1 give $T_C = 347$ K which represents the Curie temperature of our powder sample of $Fe_{0.5}Cu_{0.5}Cr_2S_4$, a value consistent with numbers reported in the literature. In [2] the Curie temperature for a single crystalline specimen was given as 275 K. Recently we have grown single crystalline $Fe_{0.5}Cu_{0.5}Cr_2S_4$ using chlorine free technology. The Curie temperature was found to be 335 K, which is close to the value of the polycrystalline material. The extrapolation to higher temperature values of either the local field, the hyperfine field (see [20]) or the magnetization is problematic. As demonstrated, for example,

in figure 3, this results in too low a transition temperature. The reason is the rather slow reduction of magnetization around the transition point. Most likely this indicates an inherently weakly inhomogeneous phase transition.

5. Conclusions

We have shown by μSR spectroscopy the existence of a spin reorientation transition in the sulfur spinel $Fe_{0.5}Cu_{0.5}Cr_2S_4$ around 100 K which has not been detected previously. A comparison with Mössbauer data on the same sample indicates that the Cr sublattice may primarily be involved. The present result is of relevance with respect to the more complex magnetic behavior of $FeCr_2S_4$. Further μSR studies in this direction are planned.

Acknowledgments

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References

[1] Ramirez A P, Cava R J and Krajewski J 1997 *Nature* **386** 156
[2] Fritsch V, Deisenhofer J, Fichtl R, Hemberger J, Krug von Nidda H-A, Mücksch M, Nicklas M, Samusi D, Thompson J D, Tidecks R, Tsurkan V and Loidl A 2003 *Phys. Rev.* B **67** 144419
[3] Siratori K and Kita E 1980 *J. Phys. Soc. Japan* **48** 1443
[4] Hemberger J, Lunkenheimer P, Fichtl R, Krug von Nidda H-A, Tsurkan V and Loidl A 2005 *Nature* **434** 364
[5] Yamasaki Y, Miyasaka S, Kaneko Y, He J-P, Arima T and Tokura Y 2006 *Phys. Rev. Lett.* **96** 207204
[6] Weber S, Lunkenheimer P, Fichtl R, Hemberger J, Tsurkan V and Loidl A 2006 *Phys. Rev. Lett.* **96** 157202
[7] Sushkov A B, Tchernyshyov O, Ratcliff W, Cheong S W and Drew H D 2005 *Phys. Rev. Lett.* **94** 137202
[8] Hemberger J, Rudolf T, Krug von Nidda H-A, Mayr F, Pimenov A, Tsurkan V and Loidl A 2006 *Phys. Rev. Lett.* **97** 087204
[9] Hemberger J, Krug von Nidda H-A, Tsurkan V and Loidl A 2007 *Phys. Rev. Lett.* **98** 147203
[10] Rudolf T, Kant Ch, Mayr F, Hemberger J, Tsurkan V and Loidl A 2007 *New J. Phys.* **9** 76
[11] van Stapele R P 1982 *Ferromagnetic Materials* vol 3, ed E P Wohlfarth (Amsterdam: North-Holland) p 606
[12] Fritsch V, Hemberger J, Büttgen N, Scheidt E-W, Krug von Nidda H-A, Loidl A and Tsurkan V 2004 *Phys. Rev. Lett.* **92** 116401
[13] Krimmel A, Mücksch M, Tsurkan V, Koza M M, Mutka H and Loidl A 2005 *Phys. Rev. Lett.* **94** 237402
[14] Krimmel A, Mücksch M, Tsurkan V, Koza M M, Mutka H, Ritter C, Sheptyakov D V, Horn S and Loidl A 2006 *Phys. Rev.* B **73** 014413
[15] Bergman D, Alicea J, Gull E, Trebst S and Balents L 2007 *Nat. Phys.* **3** 487
[16] Lee S-H, Broholm C, Ratcliff W, Gasparovic G, Huang Q, Kim T H and Cheong S-W 2002 *Nature* **418** 856
[17] Haake G and Beegle L C 1967 *J. Phys. Chem. Solids* **28** 1699
[18] Fichtl R, Fritsch V, Krug von Nidda H-A, Scheidt E-W, Tsurkan V, Lunkenheimer P, Hemberger J and Loidl A 2005 *Phys. Rev. Lett.* **94** 027601
[19] Lang O, Felser C, Seshadri R, Renz F, Kiat J-M, Ensling J, Gütlich P and Tremmel W 2000 *Adv. Mater.* **12** 65
[20] Klenczár Z, Kuzman E, Homonnay Z, Németh Z, Virág I, Kühberger M, Gritzner G and Vértes A 2005 *Physica* B **358** 93
[21] Palmer H M and Greaves C 1999 *J. Mater. Chem.* **9** 637
[22] Arsenau D J, Hitti B, Kreitzmann S R and Whidden E 1997 *Hyperfine Interact.* **106** 277
[23] Kalvius G M, Noakes D R and Hartmann O 2001 *Handbook on the Physics and Chemistry of Rare Earth* vol 32, ed K A Gschneidner *et al* (Amsterdam: Elsevier Science) p 55ff
[24] Lee S L, Kilcoyne S H and Cywinski R (ed) 1999 *Muon Science* (London: IOP)
[25] Davis E A and Cox S F 1996 *Protons and Muons in Material Science* (London: Taylor and Francis)
[26] Karlsson E 1995 *Solid State Phenomena as seen by Muons, Protons and Excited Nuclei* (Oxford: Oxford University Press)
[27] Schenck A 1985 *Muon Spin Rotation Spectroscopy* (Bristol: Hilger)
[28] Slichter C P 1978 *Principles of Magnetic Resonance* (Berlin: Springer)
[29] Hartmann O, Wäppling R, Karlsson E, Kalvius G M, Asch L, Litterst F J, Aggarwal K, Münch K H, Gygax F N and Schenck A 1990 *Hyperfine Interact.* **64** 369
[30] Hartmann O, Karlsson E, Wäppling R, Asch L, Henneberger S, Kalvius G M, Kratzer A, Klauß H-H, Litterst F J and de Melo M A C 1994 *Hyperfine Interact.* **85** 251
[31] Meier P F, Kündig W, Patterson B D and Ruegg K H 1978 *Hyperfine Interact.* **5** 311
[32] Yaouanc A J, Budnik J, Albert E, Hamma M, Weidinger A, Fruchart R, L'Heritier Ph, Fruchart D and Wolfers P 1987 *J. Magn. Magn. Mater.* **67** L286
[33] Ok H N, Baek K S, Lee H S and Kim C S 1990 *Phys. Rev.* B **41** 41
[34] van der Woude F 1966 *Phys. Status Solidi* **17** 417
[35] Graf H, Hofmann W, Kündig W, Meier P F, Patterson B D and Rodriguez A 1978 *Solid State Commun.* **25** 1079
[36] Dalmas de Réotier P, Gubbens P C M and Yaouanc A 2004 *J. Phys.: Condens. Matter* **16** S4687
[37] Dalmas de Réotier P and Yaouanc A 1997 *J. Phys.: Condens. Matter* **9** 9113
[38] Yaouanc A and Dalmas de Réotier P 1991 *J. Phys.: Condens. Matter* **3** 6195