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NEUTRON SCATTERING STUDY OF SPIN CORRELATIONS IN THE HIGHLY FRUSTRATED SYSTEMS $CsNiFeF_6$ and $CsMnFeF_6$

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Abstract

We have performed a quasielastic neutron scattering study on single crystals of the highly frustrated systems $CsNiFeF_6$ and $CsMnFeF_6$ in order to determine the spin correlations which are responsible for the strong magnetic diffuse scattering previously observed on a powder sample of $CsMnFeF_6$. It is found, that in zero field, the diffuse scattering is strongly anisotropic in the [100], [011] plane studied. The diffuse intensity follows the Brillouin zone boundary, but peaks strongly around the (002), (111) and (220) Bragg reflections. Application of a magnetic field perpendicular to the 1,0,0 , 0,1,1 -plane reduces the magnetic scattering significantly. A qualitative interpretation of the experimental findings will be given.

Introduction

The spinglass state can be considered a new type of ordered phase, despite the still ongoing discussion whether or not a well defined phase transition marks the onset of this new state. While there is a wealth of experimental data on spinglass systems of the dilute alloy type a consistent theoretical understanding has not been achieved yet (see a series of other papers in this volume). There is however another approach to spinglass behaviour, which might be easier, even to treat theoretically. This approach is based upon the concept of frustration of the magnetic moments and some randomness in the system. This concept can be applied to systems very different from the dilute alloys, which are often considered the prototype spinglass systems. This is because frustration can be caused by simple structural reasons in a regular crystal. Randomness might be introduced into the system by randomly distributing magnetic ions on equivalent lattice sites yielding random exchange, random anisotropy or random S or a mixture of all these random quantities. The realization of such systems as magnetic insulators has another conceptual advantage: the magnetic interaction is of short range type and thus the theoretical treatment becomes clearer. Especially Monte Carlo simulations have been a very powerful tool to elucidate important physical features of these systems (see the paper by K. Binder in this volume). Experimentally one could hope to do more microscopic studies like neutron scattering on single crystal samples of these insulating and magnetically concentrated systems with frustration to gain more insight in the details of the spin correlations of these systems. While several studies on such systems, mostly on powder samples, have been reported, no neutron study on single crystals of such systems has been reported yet. Such studies are, however, crucial for the understanding of the spin correlations, because in such systems the magnetic ions form a regular lattice, which might have different types of correlations along different lattice directions. This can only be elucidated by studies on single crystals.

We have therefore started an extensive and detailed neutron scattering study on single crystals of substances with the following general formula $AM^{II}M^{III}F_6$, where A = K, Rb, Cs, M^{II} and M^{III} are di- or three valent transition metals. It has been shown that $CsMnFeF_6$ shows very strong magnetic diffuse scattering over a large temperature range increasing with decreasing temperature down to 75 K from where on the diffuse scattering stays constant [1]. At 27 K susceptibility measurements indicate a phase transition, while with neutrons this phase transition can hardly be detected. Furthermore the application of a small magnetic field makes disappear even these very weak indications of the phase transition [2]. For $CsNiFeF_6$ only the susceptibility results are available indicating a phase transition at 7 K[3].

In this paper we shall discuss the results of a quasielastic neutron scattering study of the short range order (SRO) in $CsMnFeF_6$ and $CsNiFeF_6$ with and without magnetic field.

Sample, Experimental

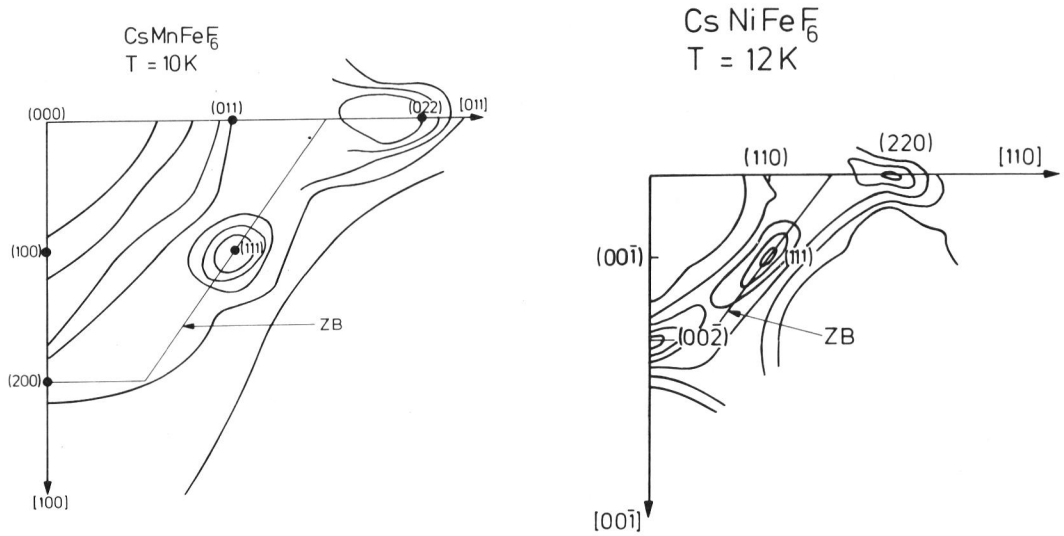
$CsMnFeF_6$ and $CsNiFeF_6$, both crystallize in the modified pyrochlor structure, space group Fd 3 m with the lattice constants a = 10.522 Å and 10.361 Å. In this structure the different transition metal ions are randomly distributed over the 16c sites. Important for the magnetic properties to be discussed later is that these sites form regular corner - sharing tetrahedra [4]. The single crystals used in this study were approximately 0.5 cm^3 in volume and have been produced by Dr. B. Wanklyn, Clarendon Laboratory, Oxford. These crystals were of very good quality. Because they were strongly coloured, they have been examined with respect to a possible O^{2-}-contamination, but no such contamination could be found.
The experiments have been carried out at the BER II reactor of the Hahn-Meitner-Institut using a two axis diffractometer with a multicounter system ($CsNiFeF_6$) and one with single counter ($CsMnFeF_6$). The wave length used was λ = 2.395 Å and λ = 2.156Å resp. Diffraction patterns have been collected between 5K and room temperature, having the $[0\bar{1}1]$ direction vertical. The magnetic field produced by a superconducting split pair magnet was parallel to this direction, perpendicular to the scattering plane.

Experimental Results

The most clear way to display the experimental results relevant for the discussion of the SRO is to use contour-maps for the scattered intensity in the scattering plane. In fig. 1a),b) we show two such maps for $CsNiFeF_6$ and $CsMnFeF_6$ resp. as obtained at 12 K and 10K with zero magnetic field. As the $[0\bar{1}1]$ was vertical in both cases, the scattering was recorded for a plane spanned by [100] and [011]. The first ZB is indicated as well. In both cases a smooth background (BG) has been subtracted. This BG has been estimated from measurements at low and high 2ϑ-angles for $CsNiFeF_6$, while it was measured for $CsMnFeF_6$ by using the experimental setup,but without the sample. Obviously both maps look very similar, showing a broad ridge of intensity along the Brillouin-Zone-Boundary. On top of this broad feature we see intensity concentrated around the (200), (111), (022) reciprocal space points, again in both patterns. It should be mentioned that the grid of experimental points for $CsNiFeF_6$ is much finer than the one for $CsMnFeF_6$. In $CsNiFeF_6$ we found that the intensity of this diffuse scattering increased continuously when decreasing the temperature from room temperature to 12K. During the course of our study of the $CsNiFeF_6$ we have found that

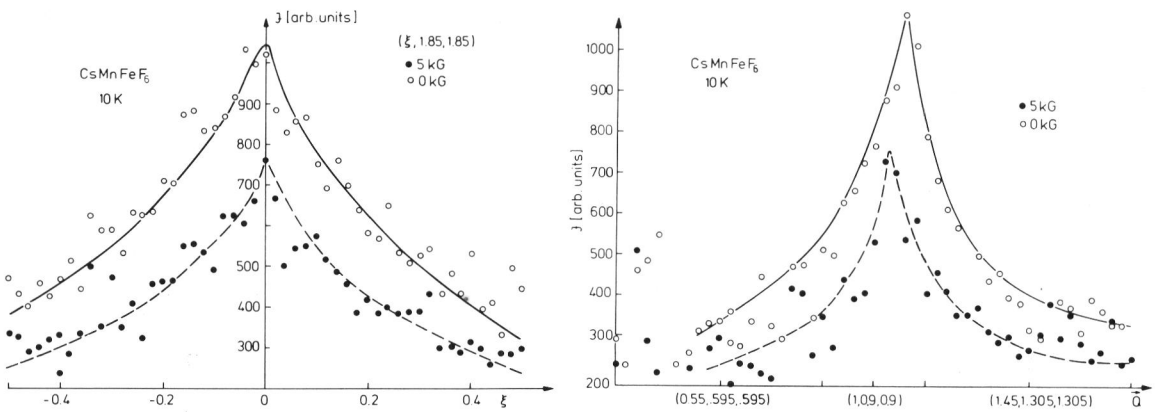
a) there is some indication that the real symmetry might be lower than Fd3m
b) there is not only diffuse scattering which increases with decreasing temperature but scattering has been found which decreases with decreasing temperature.

Because we believe that these results are not essential for the qualitative interpretation of the magnetic diffuse scattering [5], we shall not discuss these features further.



a) b)

Fig. 1: Contour maps of background corrected intensity in the scattering plane in zero field



a) b)

Fig. 2: Comparison of zero field and 5 kG-measurements at different places in reciprocal space for $CsMnFeF_6$
a) across the [011]-direction, b) along the [111] direction

As to the field dependence of the diffuse magnetic scattering, we show in fig. 2a,b two scans in reciprocal space for field H = 0 and H = 5 kG at 10 K. In both cases the magnetic field reduces the strength of the scattering without changing the shape of the profile. There are indications, that the reduction increases from [011] to [100]. It is important to note that the field was applied to the cold sample. Switching the field off did not bring back the previous intensity nor did the intensity increase when heating the sample up to 40 K and cooling down to 10 K again in zero field. No particular effort was made to observe very small intensity changes of Bragg reflections as previously reported for the $CsMnFeF_6$-powder [2]. This is because we expected extinction problems to be extreme for the big high quality crystals used in this study.

Discussion

Before we discuss the results presented here, let us recall what is known about the two systems: For $CsNiFeF_6$ susceptibility measurements are the only sources of information up to now: indication of a PT around 7K, $\Theta_p = -100$K no special features in $\chi(T)$ for $T > 7$K [3]. In $CsNiFeF_6$ the magnetic ions which occupy equivalent sites are significantly different: Ni^{2+} has a d^8-configuration yielding S=1 and $\mu \sim 2\mu_B$ while Fe^{3+} with the d^5-configuration, S = 5/2 has $\mu \sim 5\mu_B$.
More information is available for $CsMnFeF_6$: indication for a PT around 27K, $\Theta_p \approx -300$ K, no special features in $\chi(T)$ for $T > 27$K. From neutron scattering on powder exists clear evidence for SRO, which increases with decreasing temperature to 75K, from whereon it does not change anymore, not even at $T < 27$ K. There is some evidence from powder measurements that the (111) and (311)-reflections increase very slightly for $T < 27$K. This contribution disappears after application of a magnetic field and does not reappear at zero field except after warming up to $T > 80$ K and cooling down to $T < 27$K again. In $CsMnFeF_6$, both magnetic ions have the same electronic configuration d^5, thus making them magnetically equivalent with S = 5/2 and $\mu_{eff} \sim 5\mu_B$.
As far as anisotropy is concerned, nothing is known in both cases. It is very likely however that for $CsNiFeF_6$ a possible anisotropy would be stronger than for the $CsMnFeF_6$.
In order to understand the type of SRO which correponds to the maps shown in fig. 1, we start with the arrangement of the magnetic ions as found in the modified pyrochlor structure: The magnetic ions form regular tetrahedra which are linked together through common corners in such a way as to yield a triangular nearest neighbour coordination for all the magnetic ions. Since we know from the susceptibility that the dominating interaction is, not surprisingly, strongly antiferromagnetic, we are facing a system, which suffers from severe frustration, as soon as it tries to follow the strong antiferromagnetic exchange. It is easy to see what happens if we consider the case where the spins try to align antiparallel. To make the consideration easier we assume an Ising-type anisotropy, one exchange constant and identical magnetic ions. Then it is obvious that for one single tetrahedron the groundstate is characterized by 4 bounds which satisfy and 2 bounds which don't satisfy the AFM-exchange. This groundstate is fourfold degenerate, because the location of the two up- and the two down spins is unspecified. This degeneracy will very effectively decouple the corner-sharing-tetrahedra and will prevent any LRO in such a system [6]. The only ordering effect we could expect is SRO of the above type with correlations exceeding one tetrahedron falling off exponentially with distance. Such SRO yields in a neutron scattering experiment a broad ridge along the ZB, as shown in fig. 1, with a relative maximum between (200) and (111). The width of this ridge was found by Monte Carlo simulation to decrease with decreasing T [6]. No sign of peaks around (200), (111), (022) was found.
Even if this homogeneous model cannot be applied directly to the real systems studied, we expect that some principal features can be expected in the real system. The fact that the frustration prevents the appearance of a PT might

hold for the real system as well as long as higher order interactions are ineffective. We would expect that the random fields present in the real systems, like random exchange, in both systems, or, and random anisotropy and random spin would further suppress a PT, at least in zero field.
It is tempting to attribute the broad ridge along the ZB seen in the maps of fig. 1 for both systems to the SRO discussed for the homogeneous model, while the peaks around (200), (111) and (022) seem to be another type of SRO. While the SRO (I) yielding the ridge extends over one unit cell, the SRO (II) corresponding to the peaks extends over ~3 unit cells. The location in reciprocal space leads to the following spin arrangement responsible for this SRO (II): The chains of spins in planes parallel to the faces of the unit cell try to arrange in a simple + - arrangement. The appearance of SRO (II) indicates that some higher order interaction becomes effective. Thus our single crystal results suggest that in $CsMnFeF_6$ two types of SRO are present: one which is typical for the frustration in the system and one which is produced by higher order interactions, which try to overcome the frustration. Both effects should have different temperature regions, but an experimental proof needs further studies. The field effects reported by Bevaart et al. [2] suggested that the field transferred the system into another metastable state which would be characteristic for a spinglass state. In this study, however, influence of the field on the SRO was not found. The results shown in fig. 2 clearly show that the diffuse scattering is affected by the field. The observed mere reduction of the scattered intensity suggests that only the scattering strength of the system is reduced by the field, while the correlations remain unchanged. Since the applied field was 5kG only, it was not expected that correlations could be changed which depend on energies of more than 100 kG. An explanation for the field induced changes would be the assumption that the spins prefer to point along a certain crystallographic direction like [100], [110], [111]. The magnetic field would then turn as many as possible spins out of the field direction. That would mean that certain possible spin directions are depopulated while others become more populated in the field than in zero field. This effect can be most easily seen for the [100] easy direction and field along one of these directions, say $[01\bar{1}]$. In this case in zero field the [100], [010] and [001] are equally populated, while in finite field [100] would be populated only. Because the neutrons see spin components perpendicular to the momentum transfer only, in this case the magnetic scattering strength would be equal (1) for scattering along [100] and [011] in zero field, while in finite field the scattering strength would be zero along [100] and 1.5 along [011]. This however is not found. If we allow the spins to point in any direction, an isotropic Heisenberg model, then the application of the field would yield an equal reduction of the scattering strength in our scattering plane of about 25%. This is in reasonable agreement with experiment, the observed difference in reduction along [100] and [011] points to the possibility, that there is some weak Ising like anisotropy preferring the cubic axis. This is in agreement with earlier predictions from Mößbauer experiments [7]. Thus we conclude that the field causes the spins to rotate. The fact that this rotation is not reversible when the field is switched off even if the temperature is increased by a factor 4 again resembles spinglass behaviour. In addition it shows that this has nothing to do with the proposed PT, because the temperatures were $T = 10\ K < 27\ K$ and $T = 40\ K > 27\ K$. However further experiments need to confirm that 75 K is indeed a special temperature for $CsMnFeF_6$ as suggested [2]. In addition such experiments on $CsNiFeF_6$ might lead to qualitatively different behaviour because $\mu_{Ni} \neq \mu_{Fe}$.

We have seen that neutron scattering studies on single crystals of $CsMnFeF_6$ and $CsNiFeF_6$ have led to a more detailed physical picture of spin correlations. Comparison with MC-simulation suggest that there is SRO due to frustration and SRO due to higher order interaction. The effect of an applied field can be traced back to a spin rotation (spin flop) of the clusters. There seems to be only a weak anisotropy with [100] as an easy axis. The nonreversibility of this rotation resembles very much spinglass behaviour charac-

terized by the fact that some spin configurations are frozen in. Thus it seems that in such compounds a realization of a highly frustrated spinglass with short range interaction can be found under certain experimental conditions.

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