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Comments

Comments are short papers which comment on papers of other authors previously published in the **Physical Review**. *Each Comment should state clearly to which paper it refers and must be accompanied by a brief abstract. The same publication schedule as for regular articles is followed, and page proofs are sent to authors.*

Comment on "Frustration effects in the disordered system $CsMnFeF_6$, studied by neutron scattering, ac susceptibility, and magnetization measurements"

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The paper commented on reports two results which contradict in two respects previous neutron diffraction experiments. The two results are (i) magnetic contributions to Bragg peaks are reported, and (ii) the diffuse neutron scattering is said to vanish in the forward direction. As the magnetic behavior of the pyrochlores $CsA^{II}B^{III}F_6$ is known to depend sensitively on whether the chemical preparation was terminated by quenching or by slow cooling, different thermal histories may explain the disagreement with respect to (i). Result (ii) in our view is certainly wrong. An estimate is given for the minimum counting rate due to the incoherent scattering inevitably produced by the sample. It is suggested that an inappropriate measuring procedure is responsible for the vanishing of the intensity at low angles.

In a recent paper,[1] Bevaart, Tegelaar, van Duyneveldt, and Steiner (BTDS) report on neutron diffraction performed on powder samples of $CsMnFeF_6$. Their results differ substantially from ours on the same subject[2–4] in two respects: (i) BTDS found magnetic contributions to Bragg peaks, whereas we found none, (ii) BTDS further found the diffuse scattering, which peaks near the (111) reflection, to vanish in the forward direction. Our data, on the other hand, indicated that the diffuse intensity passes through a minimum near $k=(2\pi\sin\theta)/\lambda\approx0.225$ Å^{-1}. It increases when going in either direction, towards the (111) peak as well as towards the primary beam (see, e.g., Fig. 1 in Ref. 4). We do not object to the susceptibility data presented by BTDS.

We first comment on point (i). BTDS state that in their control measurements using single crystals they did not observe essential differences from their powder data. But in Refs. 5 and 6 it is explicitly stated that the single-crystal studies do not allow for an unambiguous conclusion as to the existence of magnetic contributions to Bragg peaks.[5,6] The $\approx25\%$ reduction of the (111) intensity on heating from ≈4 to 70 K given in Fig. 4 of BTDS is much too large (our results indicate a weaker decrease by an order of magnitude). Additional doubts as to the reliability of the Bragg intensities arise from the lack of the (222) peak in their Fig. 2 (see the next to last paragraph of this Comment).

However, the possibility exists that the properties of the $CsMnFeF_6$ samples used by BTDS and in our work differ because of different thermal histories. A decade ago Binder[7] demonstrated that the magnetic properties of some modified pyrochlores $CsA^{II}B^{III}F_6$ depend sensitively on the thermal history of the samples. The paramagnetic Curie temperature Θ_p as well as the μ_{eff} versus T plots strongly differed for samples quenched from 750 °C to room temperature vs ones cooled at a rate of 300 K/h. Nonetheless, the x-ray powder patterns of both types of specimen were indistinguishable. These results were obtained with $CsCoCrF_6$ and $CsCoVF_6$, the only pyrochlores studied for this property.[7] It is tempting to assume that all pyrochlores $CsA^{II}B^{III}F_6$ might behave this way. Further, several slowly cooled pyrochlores have symmetries lower than cubic.[8] The wrong temperature dependence of the thermal parameters $B(\text{Mn,Fe})$ and $B_{ij}(\text{F})$ given in Table I of BTDS suggests that there are problems with the crystal structure. More importantly, the evaluation of Bragg intensities does not allow any conclusion to be drawn as to the absence of short-range order in the Mn:Fe distribution, and nonrandomness cannot be ruled out.

The thermal history of the powder sample used by BTDS is not known to us. But BTDS checked their results obtained with the powder against measurements performed on a single crystal.[1] This crystal was supplied by Dr. Wanklyn. According to Wanklyn *et al.*,[8] the crystal was flux grown by cooling a melt from 1080 to 500 °C at 2 K/h. In addition to fluorides this melt contained CsCl, and $MnCl_2$ formed during the growth.[8] Since the pyrochlores are phases $Cs_{1+x}A_{1+x}B_{1-x}F_6$ (Ref. 9) rather than stoichiometric compounds, shifts in the Mn:Fe ratio in the crystals cannot be excluded. This would tend to increase the nonrandomness in the Mn:Fe distribution which presumably has already been introduced by the slow cooling. Since BTDS rely on the statement that frustration and randomness be sufficient to bring about spin-glass behavior,[1] nonrandomness must be carefully avoided in any work intended to yield data relevant to spin-glass problems. This remark in particular applies to Ref. 10, a companion paper to Ref. 1 dealing with single-crystal work.

Our $CsMnFeF_6$ sample was prepared by Binder at 750 °C, from which temperature it was quenched. The same treatment was applied also to the $CsCrMnF_6$ sample dealt with in Refs. 2, 3, and 11. At the time of the neutron-diffraction measurement performed at the Institut Laue-Langevin (ILL), Grenoble, our $CsMnFeF_6$ sample had been stored at room temperature for ≈ 2 years.

In conclusion, with respect to point (i) we suggest that the (non)existence of magnetic long-range order, expressed in the (non)existence of magnetic contributions to Bragg peaks, might be a property depending on the thermal history of the particular samples. Within the accuracy of our experiment we did not find magnetic long-range order, a result which should apply at least to samples with random transition-metal distribution $A:B$.

The other difference between the results by BTDS and ours, i.e., point (ii), is likely to be due to an inappropriate measuring procedure. We cite the experimental details given in our previous paper:[2] neutron flux at the sample: $10^6\ \mathrm{n\,sec^{-1}\,cm^{-2}}$; sample-to-detector distance: 1.5 m; width in 2θ per channel: 0.2°; $\lambda = 2.438$ Å; measuring time per run: 2 h; sample mass: ~ 1 g.[2] The exact weight cannot be retrieved. The version of the diffractometer D1b at the Institut Laue-Langevin (ILL) used in our experiment covered only a range of 60° in 2θ, and was a precursor of the model described in Ref. 12. A copy of the latter which covers 80° in 2θ has been installed at the BER-II reactor of the Hahn-Meitner Institut (HMI) in Berlin and was used by BTDS. In our instrument the effective width of the channels normal to the scattering plane was 1.7 cm. The maximum path length of the neutrons in the detector was 11 cm (Ref. 13). The detector was filled with 770 Torr BF_3 enriched to 95% with $^{10}BF_3$. For $\lambda = 2.438$ Å the detection efficiency was 75%.[13]

These data, together with the cross sections for incoherent scattering, allow one to compute the incoherent intensity from the sample. This will be the minimum counting rate to be expected even for a magnetically fully ordered material. The diffuse intensity due to magnetic short-range order will add to this minimum rate. The shape of that additional scattering will depend on the details of the magnetic correlations present. There will be an increase in the forward scattering, as we found for $CsMnFeF_6$,[2–4] if there are ferromagnetic correlations of some importance. A nearly constant counting rate over an appreciable range of angles will result, on the other hand, if there are only antiferromagnetic correlations. This is apparently the case with $CsMnCrF_6$. Raw data, not corrected for instrumental background and collected at ambient and liquid-helium temperatures with $CsMnCrF_6$, are given in Ref. 3. The corrected data, which are plotted in Ref. 11, reveal paramagnetism at room temperature. At 4.2 K a constant low counting rate in the forward direction and a diffuse peak near the (111) nuclear reflection have been found.[11]

Counting rates tending to zero at low angles, as reported by BTDS for $CsMnFeF_6$, violate physical laws.

From the data compiled by Koester,[14] we find

$$\sigma_{\mathrm{inc}}(=\mathrm{CsMnFe}=) \approx (4.6+0.38+0.6)\ \mathrm{b}$$

$$\approx 5.6\ \mathrm{b} \cong 0.1\ \mathrm{cm^2/g},$$

without accounting for nuclear disorder effects. Assuming a completely random distribution of Mn and Fe on common sites ($16c$ in $Fd3m$) another 5.5 b are to be added twice. Further, we have to take into account the incoherent magnetic scattering. Even in a substance which is maximally ordered with respect to magnetic moments, disorder scattering occurs because the angular momentum cannot be completely aligned along the quantization direction ("zero-point motion of spins"). This effect contributes a term proportional to $S(S+1)-S^2$. Disregarding the magnetic form factor (for $2\theta = 10°$, $\lambda = 2.438$ Å, $f^2 = 1$ within a few percent for Fe^{3+} and Mn^{2+}), this effect amounts to $(\frac{2}{7})$ 21.2 b per d^5 ion, or 6.06 b per Mn^{2+} or Fe^{3+}. Thus we have

$$\sigma_{\mathrm{inc}}(=\mathrm{CsMnFe}=) = (5.6+11+12.1)\ \mathrm{b}$$

per $CsMnFeF_6$ unit. This corresponds to an incoherent cross section of 0.048 cm²/g. The theoretical counting rate, therefore, is $(10^6\ \mathrm{n\,sec^{-1}\,cm^{-2}})\ (7200\ \mathrm{sec})\ (0.048\ \mathrm{cm^2})\ [(1.7\ \mathrm{cm}\,\pi)\ (1.5\ \mathrm{m}/900)/(4\pi 2.25\ \mathrm{m^2})] \times 75\% \approx 800$ n per 2 h. At low temperatures (3 K; cf. Fig. 1 of Ref. 4) we actually find a minimum counting rate of ≈ 1200 n per 2 h. This is reasonable, since the substance is certainly not fully ordered.

No details are available to us for the experiments performed by BTDS at the BER-II reactor in Berlin. Therefore we scale the BTDS data to ours by comparing the intensity of the diffuse peak near the (111) reflection. Figure 2 of BTDS shows that their counting rate near (111) is 1.5–2 times the value in our experiment. The exact factor depends on whether merely the peak heights are compared, which are ≈ 6000 (BTDS) and ≈ 4000,[4] or whether the peak heights above the background are compared [≈ 6000 (BTDS) and ≈ 2800 (Ref. 4)]. This means that 1200–1600 counts should be expected in the forward direction for the BTDS experiment. Even on assuming a nonrandom Mn:Fe distribution, some 900 counts should still have resulted.

The result that the intensity tends to zero for a vanishing scattering angle, claimed by BTDS, cannot be correct. The error involved is outside the statistical error limits of the experiments.

This erroneous result likely is due to the poor performance of the cryostats in operation at the BER-II reactor in Berlin. The cryostat used in our experiment on the Dlb instrument at ILL, on the other hand, had been carefully designed so as to keep interference from the primary beam to as low a level as possible. This design included two features: (a) the outer vacuum jacket as well as the radiation shields have a diameter of ≈ 1 m at the level where the neutron beam passes through the cryostat; (b) a beam stop (Cd foil) is mounted inside the cryostat at the liquid-nitrogen radiation shield. At Berlin, on the other hand, the beam usually is stopped just before the multidetector (which has no collimators). Thus, there is considerable air scattering which contributes high intensities at low angles. In addition, the cryostat lines, which are huge rather than large, contribute to the total counting rate to be processed. Because of the limited time resolution of the electronics, saturation problems may result.

Saturation cannot explain, however, why the (222) nuclear reflection has not been recorded at HMI. It should appear near the (311) peak some 2° displaced towards higher angles, and clearly within the range of Fig. 2 of BTDS. It does appear in their Fig. 5, recorded at Petten with a somewhat larger wavelength. Therefore, the absence of the peak cannot be a property of the particular sample used by BTDS. The absence of the (222) reflection in their powder pattern reveals a serious deficiency in the data collection at BER-II.

In conclusion, the recent report by BTDS, which seemed to rule out the importance of ferromagnetic correlations in

$CsMnFeF_6$, does not invalidate our previous model. This described the magnetic short-range order in $CsMnFeF_6$ by an intense antiferromagnetic NN interaction, and a weaker ferromagnetic one with the NNN magnetic coordination shell (at $\sqrt{3}$ times the NN distance).[3,4] Our analysis of the high-field susceptibility peaks observed in $CsNiFeF_6$ also revealed the presence of ferromagnetic interactions (the $CsNiFeF_6$ sample was furnace cooled from 750 °C, not quenched). The two-spin model, applied to $CsNiFeF_6$ in Ref. 15, likewise applies to the field-susceptibility peaks reported for $CsMnFeF_6$ in Ref. 4.

It is a pleasure to thank Dr. P. Convert (ILL) for his fine cooperation, as well as for the communication of the relevant parameters of the prototype version of the Dlb instrument.

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[15] W. Kurtz, Solid State Commun. **42**, 871 (1982); on p. 873, it should read $\ldots Z = \sum_j \exp \cdots$; $\chi(H,T)$ instead of $\mathscr{H}(H,T) \ldots$, and $\ldots J, \chi(H,T) \ldots$; also cf. **43**, (i) (E) (1982).