Inelastic neutron scattering below 85 μeV and zero-field splitting parameters in the Fe_8 magnetic cluster

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We present the results of high-resolution inelastic neutron scattering experiments in the energy region below 85 μeV for the octanuclear iron molecular cluster Fe_8, which are relevant to the problem of determining the zero-field splitting parameters of the $S=10$ spin ground state. By using a cold-neutron backscattering spectrometer, we observed two magnetic peaks at 14.5 and at 7.5 μeV. Their position and intensity support a previous determination of the zero-field splitting parameters by neutron spectroscopy. The experimental findings are discussed in relation to very recent quantum phase interference and single-crystal electron paramagnetic resonance measurements.

We have recently reported the results of an inelastic neutron scattering (INS) experiment on the compound $[Fe_8O_2(OH)_{12}(tacn)_6]Br_8$, where (tacn) is the organic ligand triazacyclononane.[1] This system, which we will call briefly Fe_8, is constituted by weakly interacting molecular clusters of 8 Fe(III) ions, characterized by an overall symmetry D_2 and by a magnetic ground state with an effective spin $S=10$. Over the last few years, the Fe_8 has attracted a great deal of attention, after the discovery that the cluster magnetization can tunnel coherently between the two opposite directions corresponding to the pair of potential wells created by the anisotropy barrier.[2,3] The previous INS experiment was performed on the time-of-flight spectrometer IN5 at the Institute Laue-Langevin, in Grenoble, France. It enabled us to observe magnetic transitions within the ground multiplet of the cluster, and to determine accurately, from their analysis, the zero-field splitting (ZFS) parameters of the anisotropic spin Hamiltonian.

Since the symmetry of Fe_8 is lower than tetragonal, there is a considerable mixing of the $|SM\rangle$ components of the $S=10$ multiplet, particularly for $|M|\leq 6$. For this reason, the scattered intensity in the low-energy region (below about 0.3 meV) is due to the superposition of several very close transitions between the mixed states, and presents more complex features than the intensity at higher energy. Therefore, the spectra are more complex than those observed for Mn12-ac,[4] a tetragonal cluster where the occurrence of quantum tunneling of the magnetization (QTM) has also been established.[5] Although the resolution of the IN5 experiment (~ 20 μeV) was not sufficient to identify unambiguously all the allowed transitions in the low energy range, we were able to propose a set of reliable ZFS parameters, since the shape of the unresolved peaks (particularly in the interval 0.2–0.3 meV) was very sensitive to small variations of the spin Hamiltonian coefficients up to fourth order.

Higher resolution experiments are, however, necessary to disentangle the magnetic spectrum in the low-energy region and fix definitively the parameters of the effective-spin Hamiltonian. As this would be particularly important for a better understanding of QTM in molecular clusters, we decided to do a second experiment on the cold-neutron backscattering spectrometer IN10 at the Institute Laue-Langevin. We were further stimulated to perform this kind of study by recent results, for which the higher order terms in the spin Hamiltonian play a crucial role. These are: (i) the oscillations of the tunnel splitting Δ as a function of the magnetic field due to quantum phase interference[6] and (ii) high frequency electron paramagnetic resonance (EPR) in single crystals of Fe_8.[7]

In the absence of an external magnetic field, the spin Hamiltonian for Fe_8 is

$$H_S=D[S_z^2-S(S+1)/3]+E(S_x^2-S_y^2)+D'\hat{O}_4^0(S)+E'\hat{O}_4^2(S)+C\hat{O}_4^4(S), \quad (1)$$

where the fourth order spin operators are defined as

$$\hat{O}_4^0(S)=35S_z^4-[30S(S+1)-25]S_z^2-6S(S+1)+3S^2(S+1)^2 \quad (2)$$

TABLE I. The ZFS parameters (in μeV) used in the various models quoted in the text: (a) Ref. 1; (b) Ref. 6; and (c) Ref. 7 (the signs of E and E' have been chosen consistently in the three models).

	(a)	(b)	(c)
D	−25.2	−25.2	−25.4
E	−4.02	−4.02	−4.71
$10^4\ D'$	0.87	0	2.0
$10^4\ E'$	0.1	0	6
$10^4\ C$	7.4	−24.7	−9.9

$$\hat{O}_4^2(S)=\tfrac{1}{4}\{[7S_z^2-S(S+1)-5](S_+^2+S_-^2)+(S_+^2+S_-^2)[7S_z^2-S(S+1)-5]\}$$

$$\hat{O}_4^4(S)=\tfrac{1}{2}(S_+^4+S_-^4),$$

A Hamiltonian of this form was assumed both in Ref. 1 and in Refs. 6 and 7. The parameters used to fit the INS spectra in Ref. 1 are given in Table I.

The period of the oscillations of Δ measured in Ref. 6 was reproduced by using the same values of D and E as in Ref. 1, while the value of C was of opposite sign and about three times larger in absolute value (see Table I). It was also shown in Ref. 6 that the tunnel splitting is practically unaffected by variations of D' and E' with respect to the values quoted in Ref. 1, so that these parameters were assumed to be zero in the analysis of tunneling oscillations.

The best fit of the EPR spectra in Fe_8 single crystals was obtained by using the Hamiltonian, Eq. (1), together with the Zeeman term, thus considering the principal values of the g tensor as additional fitting parameters. Although the set of coefficients given in Ref. 1 guarantees a reasonable fitting, a new set of parameters is proposed in Ref. 7 on the basis of pure EPR analysis, which is also reported in Table I. Apart from a 20% greater absolute value of E, now C is of the same order as in Ref. 1, but the sign is reversed as in Ref. 6. D' and, particularly, E' are greater than found in the INS experiment, although maintaining the same sign.

In the energy range below 100 μeV, the different sets of parameters quoted in Table I give rise to the transitions reported in Table II, where the probabilities at 20 K (see Ref. 1) are given too. They are also shown in Fig. 1, from which it appears that the transition levels, in both the pairs at lower and at higher energy, swap their role passing from the INS set of parameters to the other two sets. Accidentally, the four transition energies are not too far from each other in the three models, but transitions with similar energies involve different initial and final states and have a different probability. Therefore, although the higher order terms in the Hamiltonian are relatively small, the effect of their variation is considerably enhanced on the transitions between the excited states, in the region of large mixing of the $|SM\rangle$ wave functions.

TABLE II. Calculated transition energies (in μeV) and probabilities at 20 K (between parentheses) in the three models quoted in the text: (a) Ref. 1; (b) Ref. 6; and (c) Ref. 7. The transitions are labeled by the pairs of states involved, ordered according to increasing energy.

Transition	(a)	(b)	(c)
11–12	8(0.52)	16(0.51)	21(0.49)
16–17	13(0.89)	10(0.91)	6(0.95)
13–14	52(0.24)	75(0.24)	93(0.22)
14–15	72(0.53)	58(0.58)	47(0.62)

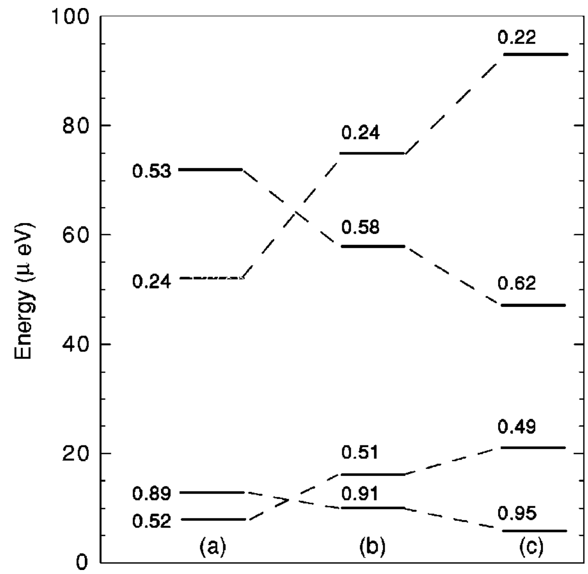

FIG. 1. Calculated transition energies (in μeV) for the three models quoted in the text: (a), Ref. 1; (b), Ref. 6; (c), Ref. 7. Corresponding transitions are joined by a broken line; the probabilities at 20 K are indicated on each level.

The IN10 inverse-geometry spectrometer is designed for inelastic scattering experiments with very high energy resolution, which can be achieved using nearly perfect backscattering both at the monochromator and at the analyzer crystals. Scans in energy transfer are performed by exploiting the thermal expansion of the monochromator to change the incident energy. The analyzer crystals are mounted on spherically hollowed backing plates with a curvature of 0.67 m^{-1}; neutrons that are backscattered from the analyzers are collected by eight ^{3}He counters placed around the sample position.

Data were taken at 20 K, using a KCl (200) monochromator and Si (111) analyzers, integrating over scattering angles ranging from 23.8° to 156.0°. The transferred energy range explored was from −2 to 85 μeV, with a resolution of about 1 μeV at the elastic position. The sample was the same as that used in the previous INS experiment.[1] The temperature of 20 K allowed a reasonable compromise between a sufficiently high probability for transitions involving the excited levels and a not exceedingly large linewidth. In spite of a large background, due to the huge number of hydrogen atoms present in the sample, two magnetic excitations have been observed.

In Fig. 2 we show the results obtained in the energy-transfer range up to 40 μeV. The data are fitted to two Gaussian line shapes, with a full width at half maximum of 5.4 and 7.4 μeV, centered at 7.4 and 14.8 μeV, respectively. The two peaks have intensities in the ratio of about

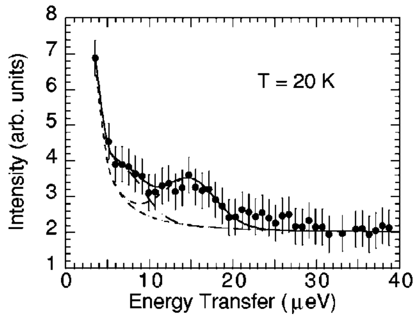

FIG. 2. The scattering intensity (in arbitrary units) vs energy transfer in the range up to 40 μeV. The experimental points are fitted to two Gaussian line shapes and a Lorentzian background (dashed-dotted line).

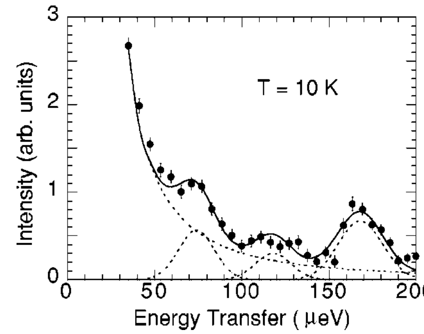

FIG. 3. Inelastic neutron scattering spectrum measured at 10 K with the IN5 chopper spectrometer at the Institute Laue-Langevin. Each excitation is represented by a Gaussian line shape (broken lines). The presence of a peak at 74 μeV is evident.

1/2. The background, shown in Fig. 2 by the dash-dotted line, has been obtained by fitting to a Lorentzian curve the spectrum recorded at 1.2 K (at this temperature the excited states are not populated and we do not expect transitions in the explored energy range).

Now, we can compare the experimental results with the predictions given for the different sets of ZFS parameters that have been proposed. Looking at Table II, it appears that the most intense peak is expected at 13 μeV from the INS set of parameters [model (a)], and at 10 and 6 μeV from the parameters of Ref. 6 [model (b)] and Ref. 7 [model (c)], respectively. Besides, the presence of magnetic scattering around 7.5 μeV, with an intensity about half that of the main peak, gives further support to the interpretation based on the previous INS results. In fact, if the main peak observed at 14.8 μeV could be identified with the transition predicted at 16 μeV in model (b), or at 21 μeV in model (c), a much more intense transition should be observable at 10 or 6 μeV, respectively, in models (b) and (c).

In the energy region from 40 up to 85 μeV (not shown in Fig. 2), we did not find evidence of the peaks at 58 and 47 μeV calculated from models (b) and (c), respectively. Following model (a), a transition at $\sim$72 μeV is expected. A slight enhancement of the intensity around 74 μeV was detected in one counting round, but not clearly confirmed by averaging on all the rounds, due to the high background and the large statistical error. However, as shown in Fig. 3, a peak was found at this energy in the IN5 experiment,[1] on the tail of the elastic peak. The fact that this excitation is not clearly seen in the present experiment is not surprising, since its intensity at 20 K is still below the sensitivity we had above 70 μeV. On the other hand, the peak expected from model (b) at 75 μeV has too low a relative probability to be compatible with the IN5 result.

In conclusion, the magnetic contribution to the neutron scattering cross section in the region up to 40 μeV gives new evidence in support to the set of ZFS parameters given in Ref. 1. With regard to model (b), it was already mentioned in Ref. 6 that non-negligible contributions to Δ come from terms in the spin Hamiltonian of order higher than four. Therefore, the best fit value of C obtained in Ref. 6 could be an ''effective value'' accounting for these other terms. The EPR results in Ref. 7, although in principle very accurate, are obtained in the asymptotic high magnetic field region, where the sensitivity to ZFS is not comparable with that of a low or zero-field spectroscopy. We have proposed a new INS experiment under magnetic field, in order to study the behavior of the transitions in low field in the energy range up to $\sim$700 μeV. This experiment should provide enough information to obtain a unique description of the anisotropy in this system. Another experiment is planned to examine the intermultiplet transitions. Once the energy splitting between the first few multiplets is determined accurately, it will be meaningful to look at the effects of mixing between different S wave functions, particularly on the low energy transitions between the excited states of the ground multiplet.

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