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HAL Id: jpa-00214095
https://hal.archives-ouvertes.fr/jpa-00214095
Submitted on 1 Jan 1971

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MAGNETIC BEHAVIOR
OF THE TWO-DIMENSIONAL ANTIFERROMAGNET BaFeF₄

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Résumé. — Les résultats de mesures de susceptibilité magnétique, de diffraction de neutrons et d'effet Mössbauer sur BaFeF₄ sont caractéristiques d'un antiferromagnétique à 2 dimensions. Les courbes de susceptibilité magnétique présentent un maximum large vers 80 °K, suivi d'une diminution rapide de $x$ le long de l'axe b à des températures plus basses. La structure magnétique est faite de couches plissées (010) où les moments plus proches voisins ont un couplage antiparallèle. Les moments sont alignés dans la direction [010] et ont une valeur de 4.2 ± 0.2 μB, et l'interaction nette entre plans adjacents est nulle. Pour 0.80 ≤ $T/T_N$ < 0.985 les champs hyperfins suivent une loi en $(T-T_N)^{β}$ avec $β$ = 0.168 ± 0.005 et $T_N$ = 54.2 °K.

Abstract. — The results of magnetic susceptibility, neutron diffraction and Mössbauer effect measurements on BaFeF₄ are characteristic of a two-dimensional antiferromagnet. The magnetic susceptibility curves have a broad maximum at about 80 °K followed at lower temperatures by a rapid decrease in $x$ along the b axis. The magnetic structure consists of puckered (010) layers, within which nearest neighbor moments are coupled antiparallel. The moments are directed along [010] and have a magnitude of 4.2 ± 0.2 μB, and the net interaction between adjacent planes is zero. From about 0.80 ≤ $T/T_N$ < 0.985 the hf fields follow a $(T-T_N)^{β}$ law with $β$ = 0.168 ± 0.005 and $T_N$ = 54.2 °K.

Recently, the isostuctural group of fluorides [1], BaMF₆, where M is a divalent 3d transition-metal ion (Mn, Fe, Co, Ni), have been shown to possess interesting piezoelectric [1], ferroelectric [2], and antiferromagnetic [1, 3, 4] properties. The crystals are orthorhombic at room temperature [1] (point symmetry 2mm) and consist [3, 4] of puckered (010) sheets of MF₆ octahedra, linked along the b axis by nonmagnetic Ba²⁺ ions. Measurements [3, 4] on the Mn and Ni compounds suggest that two-dimensional magnetic behavior is to be expected. The compound BaFeF₄ has been chosen to study this behavior, because magnetic susceptibility and neutron-diffraction measurements may be combined with Mössbauer-effect (ME) studies of Fe⁵⁷ in this material.

The samples of BaFeF₄ were synthesized from the melt as described previously [1]. Magnetic susceptibility measurements were made in a vibrating sample magnetometer. Powder neutron diffraction data were obtained at 4.4 °K and 69.9 °K with neutrons of wavelength 1.02 Å. The Mössbauer absorption spectra were obtained in a standard transmission geometry with a conventional constant acceleration spectrometer using a Co⁵⁷(Pd) source with powder and single crystal absorbers.

Magnetic susceptibility curves in BaFeF₄ are given in figure 1. Broad maxima occur at 80 ± 5 °K, for $H \parallel b$, and at 65 ± 5 °K, for $H \perp b$, while the three curves have a maximum slope, $dy/dT$, at the same temperature, $T' \approx 55$ °K. The susceptibility for $H \parallel b$ decreases to an apparent Van Vleck limit,

$$\chi_{xx} = (1.0 \pm 0.2) \times 10^{-3} \text{ e. m. u./mole},$$

at 4.2 °K. Aside from anisotropy in the (010) plane, which results from the orthorhombic symmetry in this material, the behavior is similar to that reported [7] in the anisotropic two-dimensional antiferromagnets, K₂CoF₄ and Rb₂CoF₄.

At 69.9 °K, all the neutron reflections present could be indexed on the basis of the chemical cell ($a = 5.771$ Å, $b = 14.912$ Å, $c = 4.252$ Å: A 2, z orientation). A least squares refinement of the 69.9 °K intensities yielded the following parameter values (all atoms in 4(a) positions at $x, y, 0$): Ba: $-0.048, 0.153, 0$; Fe: $0.0, 0.416, 0$; F(1): $0.381, 0.463, 0$; F(2): $0.225, 0.295, 0$; F(3): $-0.237, 0.327, 0$; F(4): $0.031, 0.918, 0$. The weighted $R$ factor based on 25 reflections was 0.054. Standard errors were approximately 0.001 and 0.002 for $x$ and $y$ parameters respec-
tively. The final values are slightly different from those in BaNiF$_4$, but must be regarded as rather tentative in view of the limited amount of data.

At 4.4 K several additional magnetic peaks were present in the neutron pattern, all of which could be indexed on a unit cell doubled in the $b$ and $c$ directions. The observed magnetic intensities can be accounted for very satisfactorily by the magnetic structure in figure 2,

$$H_{in} = 174 \pm 2 \text{ kOe},$$

the quadrupole splitting [9]

$$QS = 3.00 \pm 0.02 \text{ mm.s}^{-1},$$

the asymmetry parameter $\eta = 0.20 \pm 0.05$, and the isomer shift, $IS$ (relative to the Co$^{57}$ in Pd source) $1.23 \pm 0.02 \text{ mm.s}^{-1}$. The $QS$ and $IS$ are similar to those of other divalent iron fluorides [10]. In the antiferromagnetic state the ME spectra in a single crystal with $\gamma$ rays parallel to the [010] crystallographic direction displayed a characteristic ME pattern with relative intensities close to $3:0:1:1:0:3$, indicating that the spins are aligned in the $b$ direction.

The temperature dependence of the sublattice magnetization $M(T)$ was deduced from the ME measurement of the internal fields at the iron sites. The hf field at the iron nucleus was obtained from the separation of the two pairs of lines corresponding to the ground state splitting. In the critical region it is expected that $M(T)$ will vary as

$$M(T) = M(0) D(1 - T/T_N)^{\beta},$$

where $\beta$ is the critical exponent, $D$ a reduction factor and $T_N$ the Néel temperature. Assuming that $M(T)$ for Fe$^{2+}$ is proportional to the internal field, one can replace $M$ by $H_{in}$. A least square fit of the above equation to the data in which $\beta$, $T_N$ and $D$ are treated as independent variables is shown in figure 3. From about

![Image of a diagram](image-url)

**Fig. 2.** Magnetic structure of BaFeF$_4$ showing three successive (010) layers. Open and closed circles depict oppositely directed moments along the $b$ axis. Small numerals denote height in units of 0.01. Only Fe ions are shown.

which is also that found in BaNiF$_4$ [4]. The moments lie along the $b$ axis, as also demonstrated by the ME data, and have a magnitude of $4.2 \pm 0.2 \mu_B$ per Fe$^{2+}$ ion. In this structure, nearest neighbor moments within the (010) layers are coupled antiparallel. The net interaction between adjacent layers cancels to zero as in K$_2$NiF$_4$ [8], and, therefore, the spin structure is such as to produce considerable two-dimensional behavior.

The ME spectra of powdered material in the antiferromagnetic state show a well-resolved six-lines pattern, indicating that all the iron ions are in equivalent sites in agreement with the neutron diffraction results. Detailed analysis of the low-temperature spectra shows an optimum fit when the internal magnetic field is almost parallel to the principal axis of the EFG tensor. At 4.2 K the following hf parameters have been obtained: the internal field $H_{in} = 174 \pm 2 \text{ kOe}$, the quadrupole splitting [9]

$$QS = 3.00 \pm 0.02 \text{ mm.s}^{-1},$$

the asymmetry parameter $\eta = 0.20 \pm 0.05$, and the isomer shift, $IS$ (relative to the Co$^{57}$ in Pd source) $1.23 \pm 0.02 \text{ mm.s}^{-1}$. The $QS$ and $IS$ are similar to those of other divalent iron fluorides [10]. In the antiferromagnetic state the ME spectra in a single crystal

![Image of a graph](image-url)

**Fig. 3.** Observed internal fields in BaFeF$_4$ plotted as a function of temperature. The solid line is the best fit of the data to the points from 45 K to the Néel point (see text).

$0.80 \leq T/T_N \leq 0.985$ the values for the critical parameter are: $T_N = 54.2 \text{ K}$, $D = 1.18 \pm 0.01$ and $\beta = 0.168 \pm 0.005$ (taking $H_{in}(0) = H_{in}(4.2 \text{ K})$). The value of $\beta$ in anisotropic BaFeF$_4$ is quite close to the result for K$_2$NiF$_4$ ($\beta = 0.14$), which is considered to be a typical two-dimensional Heisenberg antiferromagnet [8].

In summary, the broad maxima in $\chi$, the cancellation of interactions between planes, and the value of the critical exponent are characteristic of a two-dimensional antiferromagnet.

We are grateful to G. K. Wertheim for helpful discussions.

References

[9] Quadrupole splitting $1/2 e\eta Q (1 + \eta^2)^{3/2}$.