

Mössbauer study of CsFeBr₃

Stephen Bocquet*

Department of Physics, University of Canterbury, Christchurch, New Zealand

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⁵⁷Fe Mössbauer spectra of CsFeBr₃ between 5.8 and 294 K are reported. The quadrupole splitting is found to be negative, and it is deduced from this that the Fe²⁺ ion has a singlet ground state. A two crystal-field model fit to the temperature variation of the quadrupole splitting reveals a large temperature-independent component of -1.03 mm/s. No evidence of magnetic ordering is found in the Mössbauer spectra down to 5.8 K.

I. INTRODUCTION

Like most other ABX_3 compounds ($A = \text{Rb}$ or Cs ; B is a divalent transition-metal ion; $X = \text{Cl}$ or Br), CsFeBr₃ has the BaNiO₃ structure, with the space group D_{6h}^4 ($P6_3/mmc$).¹ It is therefore likely to have similar magnetic properties to the isostructural iron compounds CsFeCl₃, RbFeCl₃, and RbFeBr₃. These three materials, all singlet ground-state quasi-one-dimensional antiferromagnets, have been extensively studied by Mössbauer spectroscopy²⁻⁸ and other techniques; in contrast CsFeBr₃ has received little attention.

The present study was undertaken to investigate the energy-level configuration of the Fe²⁺ ion in CsFeBr₃ and to search for magnetic ordering at low temperatures.

II. EXPERIMENTAL DETAILS

CsFeBr₃ was prepared by fusing equimolar amounts of CsBr and FeBr₂ powders in a silica tube; dry HBr gas was passed through the tube during melting to exclude air and water vapor. The melt was then sealed into the tube and a single crystal was grown by the Stockbarger-Bridgman technique.

The Mössbauer spectrometer and the methods used to prepare single-crystal and powder absorbers have been described previously.⁹ A ⁵⁷Co-Rh source was used with natural iron foil calibration.

III. RESULTS AND DISCUSSION

Spectra of a powder absorber show an asymmetric doublet for all temperatures studied (5.8–294 K). The spectrum shown in Fig. 1 is typical. The average intensity ratio¹⁰ of the two lines is 0.86(2); the intensity ratio does not show any significant temperature dependence. This asymmetry is also present in the Mössbauer spectra of powder absorbers of other isomorphous iron and ⁵⁷Fe-doped cobalt compounds;^{9,11} it may be explained by nonrandom orientation of the crystallites in the absorber.

Spectra of a single-crystal absorber were obtained with the crystal c axis oriented at $\theta = 45^\circ$, 60° , and 90° to the γ -ray beam. An example with $\theta = 90^\circ$ is shown in Fig. 1. In all three cases, the relative intensity of the low-energy

line to the high-energy line is consistent with the relationship $(3 + 3\cos^2\theta)/(2 + 3\sin^2\theta)$,¹² indicating that the quadrupole splitting is negative.

No evidence of magnetic ordering was found in the Mössbauer spectra, even at 5.8 K. It should be noted that this does not entirely preclude the presence of such order; Eibschütz, Davidson, and Cox⁶ found that RbFeBr₃ ordered magnetically at 5.5 K (from neutron-diffraction measurements), but they observed zero magnetic hyperfine field in Mössbauer spectra taken at 1.5 and 4.2 K. They attributed this to a cancellation amongst the three components \mathbf{B}_L , \mathbf{B}_D , and \mathbf{B}_S of the hyperfine field.

The Fe²⁺ ions in CsFeBr₃ are located at the centers of distorted octahedra of bromide ions. The octahedra are elongated along their trigonal axes, which are parallel to the crystal c axis. The temperature variation of the quadrupole splitting $\frac{1}{2}eQV_{zz}$ (Fig. 2) was fitted to the crystal-field model to obtain parameter values for the Hamiltonian appropriate to this site symmetry:¹¹

$$H = H_{\text{octahedral}} + H_{\text{trigonal}} + H_{\text{spin orbit}}$$

$$= B_c^4 [C_0^4 + \sqrt{10/7}(C_3^4 - C_{-3}^4)]$$

$$+ (B_0^2 C_0^2 + B_A^4 C_0^4) + \lambda \mathbf{L} \cdot \mathbf{S}$$

This Hamiltonian was diagonalized in the basis of the 25 ⁵D states, as described in Ref. 11. The resulting arrange-

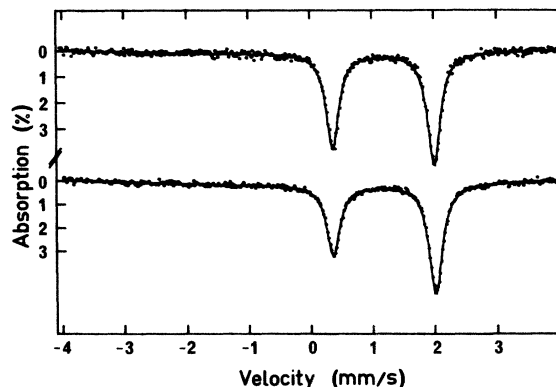


FIG. 1. Mössbauer spectra of (top) powder and (bottom) single-crystal absorbers of CsFeBr₃ at 105.5 K.

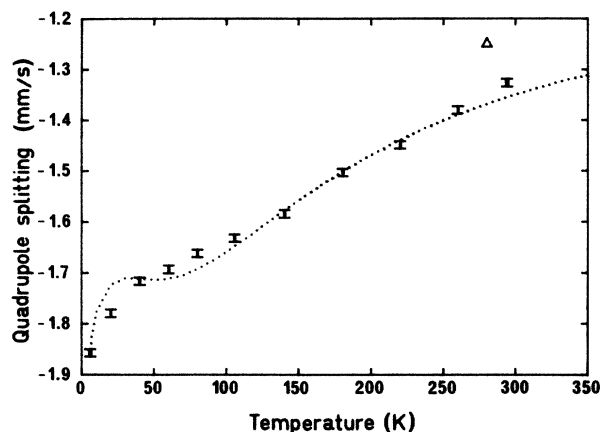


FIG. 2. Temperature variation of the quadrupole splitting in CsFeBr₃. The dotted line is a fit to the crystal-field model, with the parameter values listed in Table I. The triangle marks the measurement of Takeda, Shimada, Kanamaru, and Koizumi (Ref. 1).

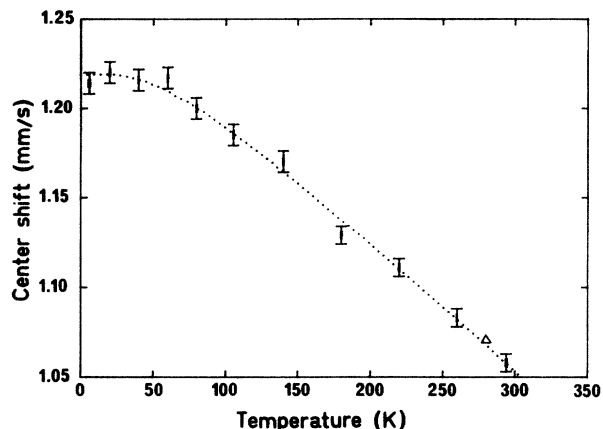


FIG. 3. Temperature variation of the center shift in CsFeBr₃. The dotted line is a fit to the Debye model. The triangle is the measurement of Takeda *et al.* (Ref. 1), corrected by 0.071 mm/s for the isomer shift of their ⁵⁷Co-Pd source relative to the ⁵⁷Co-Rh source used in this study (Ref. 19).

ment of states is the same as that in other isostructural iron and iron-doped cobalt compounds.¹¹ In particular, the ground state is a singlet and the first excited state is a doublet lying $\sim 10 \text{ cm}^{-1}$ higher in energy.

The values of the crystal-field parameters assumed or calculated in the fit are listed in Table I, along with the relative positions calculated for the eight states lying lowest in energy. The separation of the ground state and first excited state is found to be $\sim 5 \text{ cm}^{-1}$. This separation has been measured as 12 cm^{-1} in RbFeCl₃ by far-infrared spectroscopy,¹³ and calculations for RbFeCl₃,^{2-4,8,14,15} CsFeCl₃,^{2,8,14} and RbFeBr₃,⁷ based on quadrupole splitting and susceptibility data, have produced values of $12\text{--}20 \text{ cm}^{-1}$.

The cubic crystal-field parameter B_c^4 was fixed so as to produce the average splitting of 6068 cm^{-1} between the ³E and ⁵T₂ levels, determined from optical-absorption spectra of CsFeBr₃.¹⁶ $\langle r_Q^{-3} \rangle$ exceeded its free-ion value of 4.93 a.u. if it was allowed to vary in fit, so it was fixed to a value comparable to those obtained for Fe²⁺ in other materials.¹⁷ The fit reveals a large temperature-independent component (V_{zz}^0) in the quadrupole splitting, comparable with that found in Mössbauer studies of RbFeBr₃ (Ref. 7)

and RbFeCl₃.³ In all three cases, this temperature-independent component is opposite in sign and much greater in magnitude than crystal-field estimates for the lattice contribution to the quadrupole splitting;¹⁸ it has been suggested³ that it could arise from differing radial distributions for orbitals with different L_z quantum numbers in the lowest triplet (⁵T₂). The two trigonal field parameters B_0^2 and B_2^4 were found to be strongly restricted by the data, in contrast to the situation for ⁵⁷Fe-doped CsCoCl₃,¹¹ CsCoBr₃, and RbCoCl₃,⁹ where either parameter could be fixed to any value in a wide energy range, provided that the other was free to vary in the fit. The fit follows the data reasonably well (Fig. 2), although it has a local minimum and maximum in the low-temperature region which are not present in the data. Lines and Eibschütz (Fig. 13 of Ref. 7) show that these features will be removed by including an exchange term of sufficient magnitude in the Hamiltonian; however, this would require knowledge of the perpendicular and parallel susceptibility.

The center shift shows the normal variation with temperature (Fig. 3). A fit to the Debye model produced an isomer shift (0 K) value of 1.2192(1) mm/s and a Debye

TABLE I. Parameters from the crystal-field fit. The ⁵⁷Fe nuclear quadrupole moment was taken as $2.1 \times 10^{-29} \text{ m}^2$ (Ref. 15).

$\langle r_Q^{-3} \rangle$ (a.u.)	V_{zz}^0 (mm/s)	B_c^4 (cm ⁻¹)	B_0^2 (cm ⁻¹)	B_2^4 (cm ⁻¹)	λ (cm ⁻¹)	V^a (cm ⁻¹)	Energies of the lowest states relative to the ground state (cm ⁻¹) ^b			
							2,3	4,5	6,7	8
4.0 ^c	-1.026 (9)	-8454 ^c	-130.4 (2.9)	50.3 (1.0)	-60.1 (1.3)	-2599	4.5	106.6	128.1	137.5

^a V is the energy of the ground-state relative to the ⁵D centroid.

^bThe states have been numbered in order of increasing energy, with 1 being the ground state and 2,3 the doublet first excited state, etc.

^cNot varied in the fit.

temperature of 214.8(5) K.

The linewidths in the Mössbauer spectrum have been reported separately;⁹ they increase slightly with decreasing temperature, from 0.24(1) mm/s at 294 K to 0.26(1) mm/s at 5.8 K. The widths of the two lines in the quadrupole-split doublet were found to be equal, within experimental uncertainty, at all temperatures studied.

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*Present address: Department of Physics, Monash University, Clayton, Victoria 3168, Australia.

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¹⁰Here and throughout this paper, the numbers in parentheses are the uncertainties in the last digit(s) of a measurement.

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