

MÖSSBAUER SPECTRA OF TWO CUBIC FERRICYANIDES AT VERY LOW TEMPERATURES

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(Received September 8, 1972; Revised paper received November 7, 1972)

The Mössbauer spectra of two cubic ferricyanides, $\text{Cd}_3[\text{Fe}(\text{CN})_6]_2$ and $\text{Co}_3[\text{Fe}(\text{CN})_6]_2$, were measured down to 0.04 K with the aid of a $^3\text{He}/^4\text{He}$ dilution refrigerator. Somewhat unusual hyperfine structures were seen at low temperatures in the Mössbauer spectra of the 14.4 keV γ -transition of ^{57}Fe .

1. Introduction

Several ferricyanides of the type $\text{Me}_3[\text{Fe}(\text{CN})_6]_2$ are isostructural with $\text{Co}_3[\text{Co}(\text{CN})_6]_2$, having the symmetry O_h^5 ($Fm\bar{3}m$). The bimolecular unit cells are cubic, their edge being approximately 10 Å [1]. The magnetization of the ferricyanides with $\text{Me} = \text{Mn}, \text{Co}, \text{Ni}, \text{Cu},$ and Zn were measured by Bozorth *et al.* [2]. They found these complex cyanides to be ferromagnetic at low temperatures, except possibly Zn-ferricyanide. More recently, ferricyanides with $\text{Me} = \text{Mn}, \text{Co}, \text{Ni}, \text{Cu},$ and Cd were examined down to 4.2 K by the Mössbauer effect [3]. Except for cadmium ferricyanide, the Mössbauer spectra all showed a magnetic hyperfine structure at helium temperature. The ferric ion in these cyanides is in a low spin state, where $S = 1/2$. The hyperfine fields observed were between 160 and 270 kgauss. However, the lines are broad well below the assumed transition temperature, especially for cobalt ferricyanide, where there also exists a strong middle line even at 4.2 K. The shapes of the spectra were explained in Ref. [3] to be caused by combined magnetic ordering and relaxation phenomena. Therefore, it seems very profitable to extend the Mössbauer measurements of, *e.g.*, cobalt- and cadmium ferricyanide to lower temperatures.

2. Experimental details

The sample of $\text{Cd}_3[\text{Fe}(\text{CN})_6]_2$ was prepared by the reaction at 80°C of 1.1 n aqueous solution of CdCl_2 and $\text{K}_3\text{Fe}(\text{CN})_6$. The light-yellow colloidal reaction product was crystallized for 60 h in a water bath, and the precipitate was heated several times with

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distilled water, centrifuged, and then carefully washed with ethyl alcohol. The resulting compound is hygroscopic and unstable against free air. It was stored in ethyl alcohol and dried under vacuum for 20 h before the measurements. The preparation of cobalt ferricyanide was very similar to the procedure mentioned above.

A number of auxiliary analyses were performed in order to test the quality, especially of the cadmium ferricyanide sample. X-ray diffraction patterns were taken with MoK_α and CuK_α radiations. They showed that the specimen is cubic with a lattice parameter $10.66 \pm 0.01 \text{ \AA}$, in good agreement with the literature value [1]. No traces of the initial reagents were observed. However, two weak satellites were found, indicating a small quantity of KCdCl_3 or K_4CdCl_6 as an impurity. The electron microscopy pictures showed that the compound was well crystallized with crystallites of rectangular-oblate shape, from 1500 Å to 4000 Å in dimension. The thermogravimetric study indicated that there were 10 molecules of water per one $\text{Cd}_3[\text{Fe}(\text{CN})_6]_2$ molecule in fresh sample. Three of them appeared to be more strongly bound to the lattice than the rest.

Measurements of the Mössbauer spectra of the 14.4 keV radiation of ^{57}Fe were performed with the aid of a $^3\text{He}/^4\text{He}$ dilution refrigerator [4]. The absorbers were placed inside the mixing chamber of the refrigerator. The source of $^{57}\text{Co}:\text{Cu}$ was kept at 5 K during the measurements.

3. Results and discussion

Fig. 1 shows the Mössbauer spectra of $\text{Cd}_3[\text{Fe}(\text{CN})_6]_2$ at four different temperatures. A well resolved, symmetrical quadrupole doublet was observed down to 0.1 K. The value of the quadrupole splitting is then $1.13 \pm 0.02 \text{ mm/s}$, and the line width 0.6 mm/s. With decreasing temperature the lines broaden and the doublet becomes asymmetric. At 41 mK a resolved six-line spectrum on a broad background is observed.

Fig. 2 shows Mössbauer spectra of $\text{Co}_3[\text{Fe}(\text{CN})_6]_2$ at various temperatures. The quadrupole doublet becomes asymmetric at liquid nitrogen temperature. At lower temperatures a broad middle line, together with an asymmetric, badly resolved magnetically split background appears.

The asymmetries of the quadrupole doublets of $\text{Cd}_3[\text{Fe}(\text{CN})_6]_2$ and $\text{Co}_3[\text{Fe}(\text{CN})_6]_2$ can be explained by electron spin relaxation in the paramagnetic region. In an approximation of rotational symmetry, the quantum number $\pm 3/2$ of the 14.4 keV excited state must be assigned to the broader transition line [5]. Hence the quadrupole interaction in both of these compounds is negative.

For $\text{Co}_3[\text{Fe}(\text{CN})_6]_2$ the magnetic measurements gave a transition temperature 12 K (or 21 K) [2]. In our Mössbauer spectra, the possible magnetic transition is masked by the relaxation effects. In principle, it would be possible to extract from the spectrum the degree of magnetic order and the relaxation time, if the form of the hyperfine interaction is known. We have simulated the spectra by using the Blume-Tjon formalism [5] and the effective field approximation, for various relaxation times and degrees of order. We were not able to produce the pronounced middle peak deep in the ordered region. It is also peculiar that this middle line exists almost unchanged between 0.04 K and 4.2 K.

On the other hand, similar spectra are easily produced by assuming that the material is paramagnetic down to 0.04 K. Then the relaxation time should have a constant value below 4.2 K. Above this temperature the relaxation time should decrease.

For $\text{Cd}_3[\text{Fe}(\text{CN})_6]_2$ no estimates for the magnetic transition temperature are known. We first observed the relative count rate at zero velocity during the cooling of the sample. There was a marked change in the transmission near 100 mK. At this temperature the

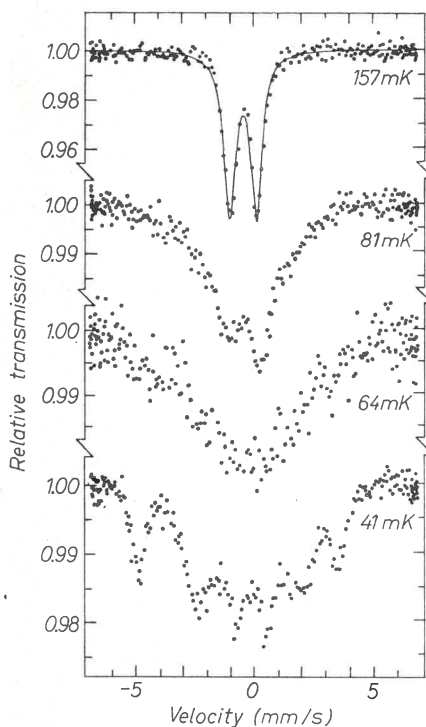


Fig. 1

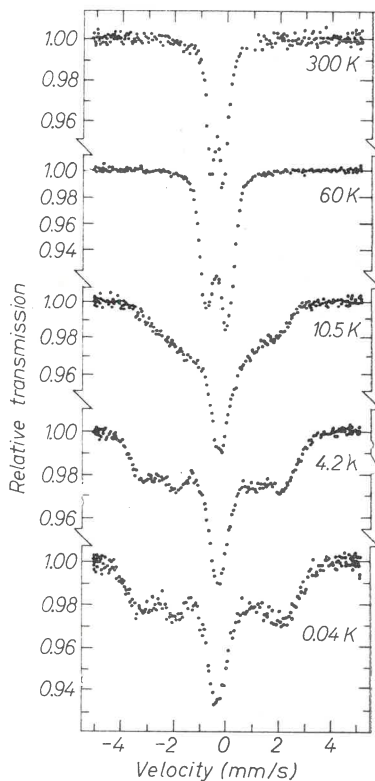


Fig. 2

Fig. 1. The Mössbauer absorption spectra of $\text{Cd}_3[\text{Fe}(\text{CN})_6]_2$ at low temperatures. The absorber thickness is 50 mg/cm^2 . At positive velocities the source and the absorber are approaching each other

Fig. 2. The Mössbauer absorption spectra of $\text{Co}_3[\text{Fe}(\text{CN})_6]_2$ at various temperatures. The absorber thickness is 50 mg/cm^2

effect of increasing relaxation time becomes observable in the Mössbauer spectrum. At 0.06 K there is, in addition to the broad middle line, a weakly resolved magnetic "six line spectrum". At 41 mK the line width of the outermost lines is about the same as the line width of the doublet above 100 mK. The positions of the six lines can be fitted by using a negative and axially symmetric electric field gradient together with an effective magnetic field of $\approx 254 \text{ kOe}$, and by assuming a value $\theta = 35^\circ$ for the angle between the directions of the fields. The absolute value of the quadrupole interaction is assumed to be temperature independent. However, the use of effective field approximation is questionable until we

have verified the magnetic ordering of this material. It is to be noted that the Hamiltonian, which consists of paramagnetic hyperfine interaction together with quadrupole interaction, will produce in the limit of slow relaxation spectra similar to those produced by the static effective field Hamiltonian. Hence for the final interpretation of the present Mössbauer spectra information about the magnetic ordering of Co- and Cd-ferricyanides is necessary. Susceptibility measurements are being made to solve this puzzle.

REFERENCES

- [1] R. W. G. Wyckoff, *Crystal Structures*, vol. 3, J. Wiley and Sons, New York 1965, p. 381.
- [2] R. M. Bozorth, H. J. Williams, D. E. Walsh, *Phys. Rev.*, **103**, 572 (1956); see also A. N. Holden, B. T. Matthias, P. W. Anderson, H. W. Lewis, *Phys. Rev.*, **102**, 1463 (1956).
- [3] A. Z. Hryniewicz, B. D. Sawicka, J. A. Sawicki, *Sov. Phys. Solid State*, **9**, 1100 (1967); *Acta Phys. Polon.*, **A37**, 811 (1970).
- [4] G. J. Ehnholm, T. E. Katila, O. V. Lounasmaa, P. Reivari, *Cryogenics*, **8**, 136 (1968).
- [5] M. Blume, *Phys. Rev. Letters*, **14**, 96 (1965); M. Blume, J. A. Tjon, *Phys. Rev.*, **165**, 446 (1968); J. A. Tjon, M. Blume, *Phys. Rev.*, **165**, 456 (1968).