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Mössbauer Effect Study of $Bi_2Fe_4O_9$

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Mössbauer parameters for pure and chromium-doped $Bi_2Fe_4O_9$ are reported above and below its magnetic ordering temperature. The substitution of chromium for a portion of the iron ions allows the unambiguous assignment of the magnetic and quadrupole split resonance lines. At room temperature the Mössbauer spectrum exhibits four lines, assignable to two quadrupole-split pairs: one pair from the tetrahedral ferric ions (IS +0.494, QS 0.960), the other pair from those which are octahedrally coordinated (IS +0.619, QS 0.383). At 77°K, well below the magnetic ordering temperature, two overlapping six-line magnetically split spectra are observed. Proper assignment gives values of 445 and 485 kOe for the effective magnetic field acting on the tetrahedral and octahedral ferric ions, respectively.

In the course of a study on the determination of site distributions of iron ions in oxide compounds with two or more different cation sites by the use of Mössbauer effect spectroscopy, we have determined the Mössbauer parameters of the compound $Bi_2Fe_4O_9$.

The crystal structure of $Bi_2Fe_4O_9$ has been determined by Niizeki and Wachi (*1*); space group *Pbam*, with trivalent iron ions occupying sites of approximately octahedral and tetrahedral coordination in equal amounts. Tutov et al. (*2*) observed a magnetic ordering temperature (T_N) of 265°K with antiferromagnetic behavior below the ordering temperature and Curie–Weiss behavior above ($\theta = -1400°K$, $\mu_{eff} = 6.09\ \mu_B$).

As our work was nearing completion, Bokov et al. (*3*) published Mössbauer data for this compound. However, we feel that our data bear reporting since we have completely resolved the Mössbauer spectra above and below the magnetic ordering temperature.

Experimental

Pure $Bi_2Fe_4O_9$ single crystals were grown in a manner analogous to that of Koizumi et al. (*4*). Reagent grade Bi_2O_3 (24.80 g, 0.5 *m*) and Fe_2O_3 (7.98 g, 0.5 *m*) were mixed together and packed in a 25-cc capacity platinum crucible. The covered, charged crucible was placed in a muffle furnace, held at 950°C for one hr and cooled at approximately 9°/hr to 750°C, then removed from the furnace. To prevent attack on the platinum crucibles, all runs were made in a flowing dry oxygen atmosphere. Chromium substitution was achieved by replacing 20 mole% of the Fe_2O_3 by Cr_2O_3 in the above formulation. After cooling to room temperature the reaction mass was washed repeatedly with hot dilute nitric acid to remove the Bi_2O_3 flux. Typical crystal size was $1 \times 1 \times 0.5$ mm. Chemical and powder X-ray diffraction analysis agrees with the formula $Bi_2Fe_4O_9$. *Anal.* Calcd: Bi, 53.2; Fe, 28.5; O, 18.3. Found: Bi, 53.8; Fe, 29.6; O, 18.2.

No attempt was made to determine the limit of chromium substitution in $Bi_2Fe_4O_9$. Although isomorphous substitution for ferric ion has been shown to occur by trivalent aluminum, gallium and (partially) manganese (*1*, *2*, *5*), the system Bi_2O_3–Cr_2O_3 does not contain a compound with this 1:2 stoichiometry (*6*). We were not able to chemically separate a small amount of unreacted Cr_2O_3 from our product, but on the basis of the Mössbauer data (*vide infra*), we estimate that about 6 at.% of the iron is substituted by chromium. Powder *X*-ray diffractometer data (Cu K_α radiation) for pure and substituted $Bi_2Fe_4O_9$ are given in Table I.

The iron-57 Mössbauer effect was measured with a Model NS-1 Mössbauer Spectrometer (Nuclear Science and Engineering Corporation, Pittsburgh, Pennsylvania) operating in the constant acceleration

TABLE I

UNIT CELL DATA

	$Bi_2Fe_4O_9$	$Bi_2Fe_4O_9$/Cr
a	7.965(4) Å	7.948(4) Å
b	8.440(4)	8.400(4)
c	5.994(4)	5.981(4)

mode. Radiation from a source of cobalt-57 (~20 mCi) diffused into palladium was detected with a gas proportional counter and collected with a 400 channel analyzer operating in time sequence scaling mode. The source and drive were calibrated against a single crystal of sodium nitroprusside (National Bureau of Standards, Standard Reference Material #725). The quadrupole splitting (QS) for sodium nitroprusside was taken as 1.7048 ± 0.0025 mm/sec (*7*). Isomer shifts (IS) are reported with respect to the zero position of this standard. Sample thickness was 30 mg/cm^2 (corresponding to 8.5 mg Fe/cm^2). The data were reduced by a computer program which performed a nonlinear least-squares fit to the product of a series of resonant absorption peaks having Lorentzian shapes superposed on a parabolic base line, a result of our particular drive geometry. All of the variables (peak position, peak height, and peak half-width) were allowed to vary independently.

Results

The Mössbauer spectrum of $Bi_2Fe_4O_9$ at room temperature is illustrated in Fig. 1. The solid curve is the computer fit to the product of a series of Lorentzian absorption peaks, the dashed curves are the individual peaks, and the circles the experimental points. An unambiguous assignment was made by measuring the Mössbauer effect of a sample in which a portion of the iron ions are replaced by chromium ions. The substitution is isomorphous, trivalent chromium substituting for trivalent iron. Of all the trivalent transition metal ions, chromium has the strongest octahedral site preference based on crystal field stabilization energies (*8*). Therefore, the Mössbauer resonance due to the octahedrally coordinated ferric ions should decrease relative to the resonance from tetrahedrally coordinated ferric ions. From the spectrum of chromium-substituted $Bi_2Fe_4O_9$ the two inner lines can be assigned to octahedrally coordinated iron. The area ratio of the octahedral to tetrahedral iron resonances for the chromium-substituted compound is 0.88 to 1.00, indicating that approximately 6 at.% of the total iron is replaced by chromium. In the undoped sample the area ratio is 1.06 to 1.00 indicating essentially equal recoil-free fractions for both sites. The Mössbauer parameters for $Bi_2Fe_4O_9$ are summarized in Table II. The data of Bokov et al. (*3*) are given for comparison (note that the pair of peaks on the high positive velocity side were not resolved by Bokov et al.); their values for isomer shift are corrected relative to the sodium nitroprusside standard.

Figure 2 illustrates the Mössbauer effect spectrum of $Bi_2Fe_4O_9$ at 77°K (the resolved individual peaks have been omitted for clarity). Note the two peaks at the center of the spectrum due to iron impurity in the beryllium windows of the dewar. The remaining spectrum—two sets of six-line spectra—is resolved by the nonlinear least-squares computer

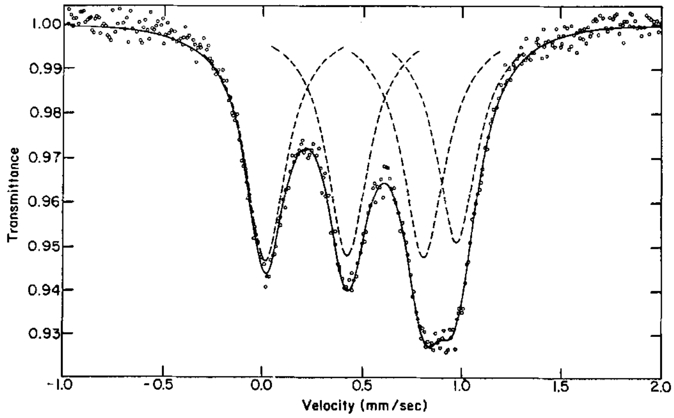

FIG. 1. Mössbauer spectrum of $Bi_2Fe_4O_9$ at room temperature. Velocity scale is relative to sodium nitroprusside. Solid line is a least-squares fit, dashed lines are the individual peaks and circles indicate the normalized data. See text for peak assignment.

TABLE II[a]

	Isomer shift[b]		Quadrupole splitting	
	This work[c]	Bokov et al.	This work[c]	Bokov et al.
Tetrahedral	+0.494	+0.43 ± 0.04	0.960	0.84 ± 0.06
Octahedral	+0.619	+0.64 ± 0.04	0.383	0.42 ± 0.06

[a] All data in mm/sec.

[b] Isomer shifts are reported relative to sodium nitroprusside.

[c] Estimated error of 0.004 mm/sec.

program (solid curve). The assignment, made with the aid of the chromium-substituted sample measured at 77°K, is indicated by the lines in Fig. 2. The resonance absorption due to tetrahedrally coordinated iron is indicated by I, that due to octahedrally coordinated iron by II.

The Mössbauer spectrum below the magnetic ordering temperature can be characterized by the parameters g_0 and g_1, the magnetic splittings of the ground and excited nuclear levels, respectively; the isomer shift; the quadrupole interaction $\frac{1}{2}e^2qQ$; and an asymmetry parameter η ($\eta = (V_{xx} - V_{yy})/V_{zz}$). Using the value of 0.09024 nuclear magnetons (*9*) for the magnetic moment of the iron nucleus, H_{eff} (the effective magnetic field acting on the iron nucleus) can be calculated from the ground state splitting. The quadrupole interaction is given by one-half the difference between the separation of lines 5 and 6 (Δ_{5-6}) and lines 1 and 2 (Δ_{1-2}), numbering from left to right in a particular six-line spectrum. Relevant parameters are listed in Table III. At each of the sites in $Bi_2Fe_4O_9$, $\Delta_{5-6} > \Delta_{1-2}$, indicating that the component of the electric field gradient in the spin direction is positive (the $I_z = \pm 3/2$ levels are raised).[1]

A closed determination of values for $\frac{1}{2}e^2qQ$ and η is valid only if the major axis of the electric field gradient tensor is either parallel or perpendicular to the direction of magnetization (*10*). An experimental check of this assumption is the calculation of H_{eff} from the splitting of the first excited nuclear level g_1 (equal to the average of the difference between Δ_{5-6} and Δ_{1-2}) which should be equal to that calculated from the ground state splitting. Calculation of H_{eff} from g_1 gives the values of 452 and 473 kOe for the tetrahedral and octahedral sites, respectively—in only fair agreement with the values calculated from g_0. This indicates that one of the axes of the electric field gradient tensor is at an angle θ (not equal to 0° or 90°) to the direction of magnetization, in which case a closed derivation of the Mössbauer parameters in the magnetically ordered region would not hold.

To resolve this problem it is necessary to know the detailed magnetic structure of $Bi_2Fe_4O_9$; a knowledge of the orientation of the direction of magnetization with the local symmetry axis and the calculation of the electric field gradient would provide the information needed to remove this ambiguity. We intend to continue investigation of $Bi_2Fe_4O_9$ by neutron diffraction to determine its magnetic structure.

In both the paramagnetic and antiferromagnetic

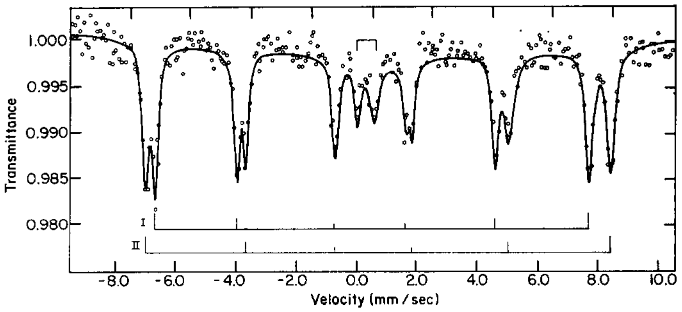

FIG. 2. Mössbauer spectrum of $Bi_2Fe_4O_9$ at 77°K. Velocity scale is relative to sodium nitroprusside. Solid line is the least-squares fit, circles are the normalized data. I indicates the six-line spectrum due to tetrahedral iron, II to octahedral iron.

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[1] Using the normal sign convention, see e.g., G. K. WERTHEIM, "Mössbauer Effect, Principles and Applications," Academic Press, New York, 1964.

TABLE III

MÖSSBAUER PARAMETERS AT 77°K

	Tetrahedral	Octahedral
IS (mm/sec)[a, b]	+0.458	+0.597
g_0 (mm/sec)	5.28	5.74
g_1 (mm/sec)	3.05	3.19
g_0/g_1	1.73	1.80
H_{eff}(kOe)	445 ± 3	484 ± 3

[a] Relative to sodium nitroprusside.

[b] Estimated error of ±0.006 mm/sec.

regions unambiguous assignments of the Mössbauer spectrum of $Bi_2Fe_4O_9$ has been made with the aid of chromium-substituted material, in which the chromium preferentially enters the octahedrally coordinated site. A closed derivation of all of the parameters is shown not to be feasible in the magnetically ordered region without the knowledge of the magnetic spin structure.

Acknowledgment

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References

1. N. NIIZEKI AND M. WACHI, *Z. Kristallogr.* **127**, 173 (1968).
2. A. C. TUTOV, I. E. MYL'NIKOVA, N. H. PARFENOVA, V. A. BOKOV, AND S. A. KIZHAER, *Sov. Phys. Solid State* **6**, 963 (1964).
3. V. A. BOKOV, G. V. NORIKOV, V. A. TRUKHTANOV, AND S. I. YUSHCHUK, *Sov. Phys. Solid State* **11**, 2324 (1970).
4. H. KOIZUMI, N. NIIZEKI, AND T. IKEDA, *Jap. J. Appl. Phys.* **3**, 495 (1964).
5. K. MASUNO, *Nippon Kagaku Zasshi* **88**, 726 (1967).
6. K. MASUNO, *Nippon Kagaku Zasshi* **90**, 1122 (1969).
7. R. W. GRANT, R. M. HOUSLEY, AND U. GONSER, *Phys. Rev.* **178**, 523 (1969).
8. D. S. MCCLURE, *J. Phys. Chem. Solids* **3**, 311 (1957).
9. P. R. LOCHER AND S. GESCHWIND, *Phys. Ref. A.* **139**, 991 (1965).
10. S. CHANDRA, Ph.D. Thesis, Boston University, 1967, unpublished.