FIZIKA 5 (1973) 145–153

STUDY OF $Bi_2Fe_4O_9$ BY MÖSSBAUER EFFECT

D. HANŽEL and A. MOLJK

Institute »Jožef Stefan«, Ljubljana and the Faculty of Science and Technology, Ljubljana

Received 11 July 1973

Abstract: The antiferromagnetic $Bi_2Fe_4O_9$ was studied between 8 and 550 K by the use of Mössbauer effect. Transition temperature was determined at $T_N = 253 \pm 3$ K, while effective magnetic field, extrapolated to 0 K, amounts to 535 ± 5 kG for actahedral and to 485 ± 5 kG for tetrahedral iron sites. The temperature dependence of the sublattice magnetization does not agree satisfactorily with the Brillouin curve for $S = 5/2$. In the region $0.76 < T/T_N < 0.97$, the sublattice magnetization is represented as $M(T) = M(O)\, D\,(1 - T/T_N)\,\beta$ with $\beta_{octa} = 0.29$ and $\beta_{tet} = 0.31$. From the quadrupole splitting above T_N and from the calculated field gradient, nuclear quadrupole moment of the excited state of iron on octahedral site is estimated as $(^{57}Q) = 0.16 \pm 0.03$ b.

1. Introduction

The crystal structure of $Bi_2Fe_4O_9$ determined by Niizeki and Wachi[1] belongs to the orthorombic system and to the space group Pbam with lattice constants $a = 7.905$°A, $b = 8.428$°A and $c = 6.005$°A. Iron ions occupy tetrahedral and octahedral sites in equal concentrations. $Bi_2Fe_4O_9$ behaves as antiferromagnetic[2,3]. From the magnetic susceptibility measuremets by A. G. Tutov et al.[2] transition temperature was determined at 265 K, while from the Mössbauer effect investigations by Bokov et al.[4], Neel temperature was established at 256 K. Bokov et al.[5] also came to the conclusion that the tetrahedral iron spins lie almost in the *ab* plane. Temperature dependence of the sublattice magnetization given by Bokov[4] is the same for both iron sites above 180 K.

In this work a study of $Bi_2Fe_4O_9$ by Mössbauer effect in the range from 8—550 K is reported and additional evidence given for temperature dependence of the sublattice magnetization particularly in the region around the Neel temperature. Further an estimate is made for the nuclear quadrupole moment of the excited state of ^{57}Fe on the base of the measured values for the quadrupole splitting in paramagnetic state and of the calculated values of the electric field gradient for both iron sites.

2. *Experimental details*

Mössbauer measurements were performed on powdered samples of $Bi_2Fe_4O_9$ obtained by standard ceramic technique[6]. Absorbers consisted of 4 mg/cm^2 of ^{57}Fe thick layers of sample between two Be windows. The source of ^{57}Co in Pd matrix was kept at room temperature during the measurements. A krypton--methan proportional counter was used for detection of 14.4 keV gamma radiation.

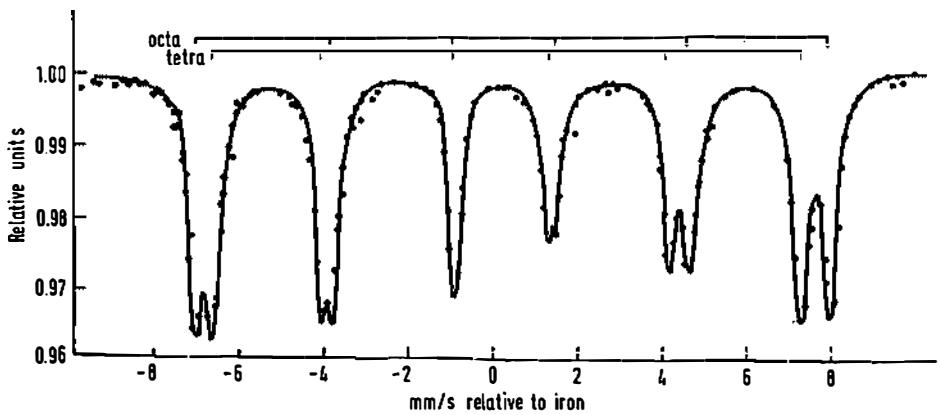

Fig. 1. Mössbauer spectrum of powdered $Bi_2Fe_4O_9$ at 76 K taken with a source of ^{57}Co in the Pd matrix.

Spectra were taken on 512 channel analyzer operated in time mode by use of the constant acceleration electromechanical drive. The velocity scale was calibrated with Fe_2O_3 and with metallic iron, which was also used as reference point for the determination of the isomer shift. The Mössbauer parameters were calculated by the use of Lorentzian lines fed to the experimental spectra for $Bi_2Fe_4O_9$.

3. *Results and discussions*

In Fig. 1 typical spectrum for antiferromagnetic state of $Bi_2Fe_4O_9$ is given. The solid curve is drawn as least square fit to ten Lorentzian lines. In Fig. 2 spectrum for paramagnetic state is represented. The assignment of the lines to the iron nuclei in octahedral and tetrahedral sites (bar diagrams) was performed by use of results of Kostiner and Schoemaker[7] who verified contribution of both sites by partial substitution of the Fe^{3+} ions by diamagnetic Cr^{3+} ions.

Below the transition temperature, spectra are characteristic for combined electric and magnetic hyperfine coupling. Except in the range close to transition temperature the quadrupole splitting represents a small perturbation only of the magnetic nuclear energy level. Thus spectra were analysed in conventional manner. The effective magnetic field was obtained from the ground state splitting, the isomer shift from the relationship $\delta = (1/4)(1 + 2 + 5 + 6)$ and the quadrupole interaction parameter ΔS from the difference $(6-5) - (1-2)$, where the numbers refer to the positions of the corresponding lines for octahedral and tetrahedral sites. These three parameters are plotted against the temperature in

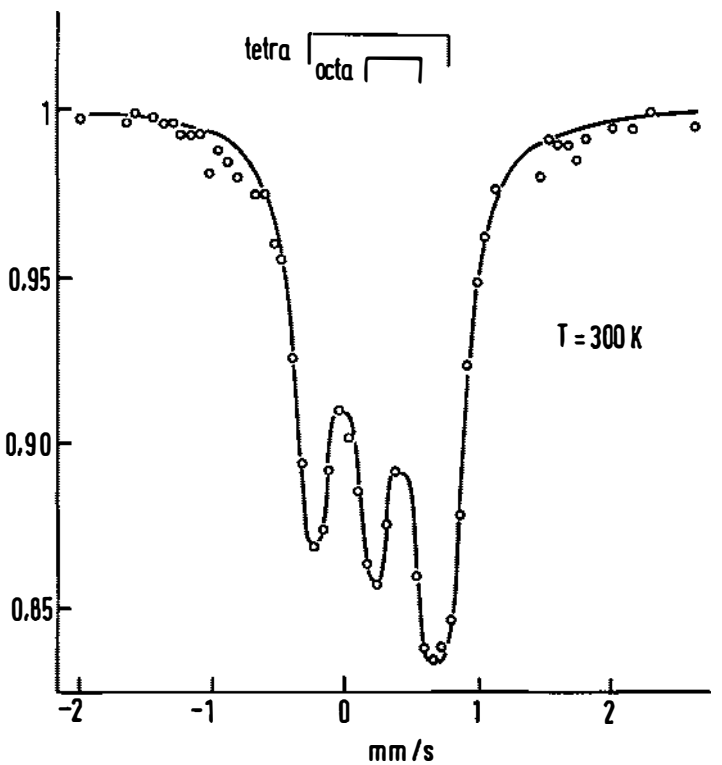

Fig. 2. Mössbauer spectrum of $Bi_2Fe_4O_9$ at 300 K.

Figs. 3, 4 and 5 for ferric ions on octahedral and tetrahedral sites. Due to the decrease of the hyperfine magnetic field and to the coallescence of the two patterns near the Neel temperature the effective magnetic field was obtained from the splitting between outer lines 1 and 6. The measured values at 8 K are: $H_{okt} = 530$ kG, $H_{tet} = 485$ kG. Intensities of effective magnetic fields extrapolated to 0 K amount to 535 ± 5 kG for octahedral and to 485 ± 5 kG tetrahedral iron sites. There values seem to be characteristic for ferric ions as they appear in garnets and spinels[8] with similar ion sites.

Neel temperature found by extrapolation of the hyperfine fields in Fig. 3 is estimated to be $T_N = 253 \pm 2$ K. Transition temperature T_N was also determined by the thermal scanning procedure. The middle peak in the spectrum at $T = 255$ K

of Fig. 6 corresponding to octahedral iron in paramagnetic state is nearly centered on zero velocity. In antiferromagnetic state this velocity lies approximately between the inner two absorption lines. Thus the transition from antiferromagnetic to paramagnetic state can be investigated by monitoring the counting rate at zero velocity as a function of temperature. As shown in Fig. 7 change in counting rate appears in the range of about 6 K. So the transition temperature is determined as 253 $\pm$ 3 K which is in accordance with the result of Bokov et al[4].

An attempt to describe the temperature dependence of the hyperfine field in Fig. 3 by a Brillouin function of $S = 5/2$, with $T_N = 253$ K and $H_{\text{octa}}(0) = 535$ KG and $H_{\text{tet}}(0) = 485$ KG does not give satisfactory results for the both iron sites.

In the critical region sublattice magnetization is expected to follow the relationship[9]

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

Assuming that the $M(T)$ is proportional to the effective magnetic field for Fe^{3+} ions, a least square fit of the data for effective magnetic field to above equation is made. Treating critical exponent β, Neel temperature T_N, and reduction factor D as independent variables, we obtain in the temperature range $0.76 < T/T_N < 0.97$ following results

$$\beta_{\text{oct}} = 0.29, \quad D_{\text{oct}} = 1.09, \quad T_N = 253 \text{ K},$$

$$\beta_{\text{tet}} = 0.31, \quad D_{\text{tet}} = 1.18, \quad T_N = 253 \text{ K}.$$

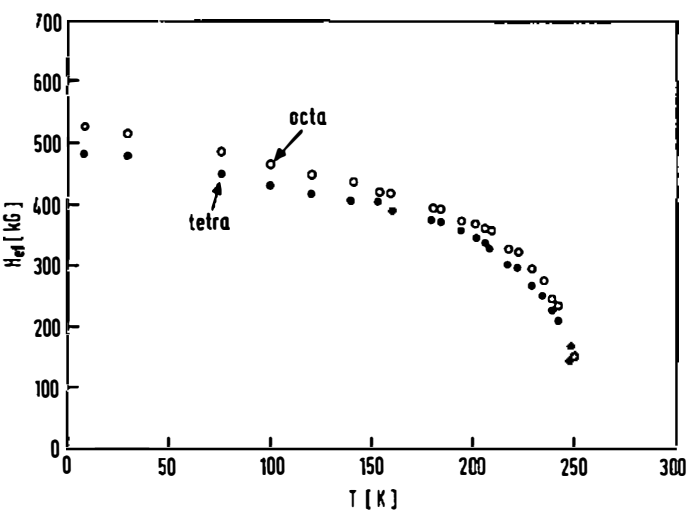

Fig. 3. Temperature dependence of the effective magnetic field at ^{57}Fe nuclei in octahedral and tetrahedral sublattice sites.

The values for critical exponent β are near to 1/3 power law of temperature dependence for sublattice magnetization predicted by two cluster approximation and by the Random phase form of Green function theory[9].

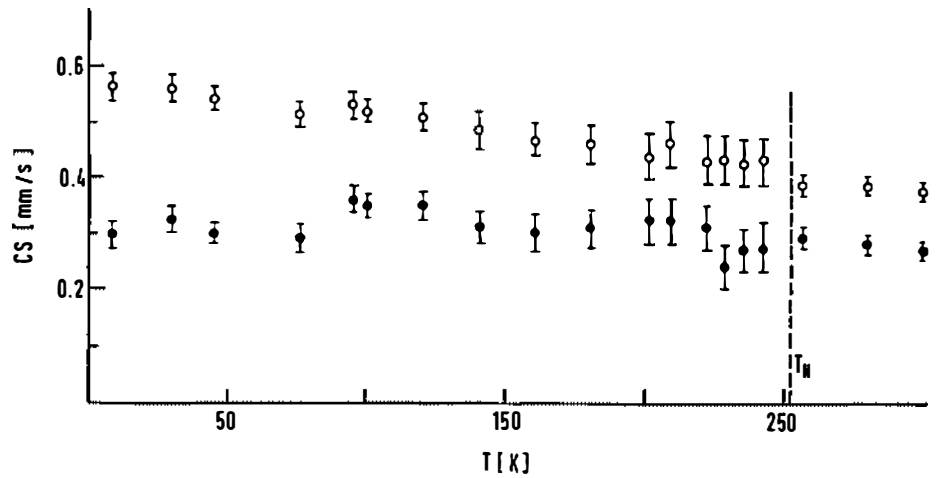

Fig. 4. Temperature dependence of the isomer shift relative to metallic iron for ^{57}Fe at octahedral and tetrahedral sites in $Bi_2Fe_4O_9$.

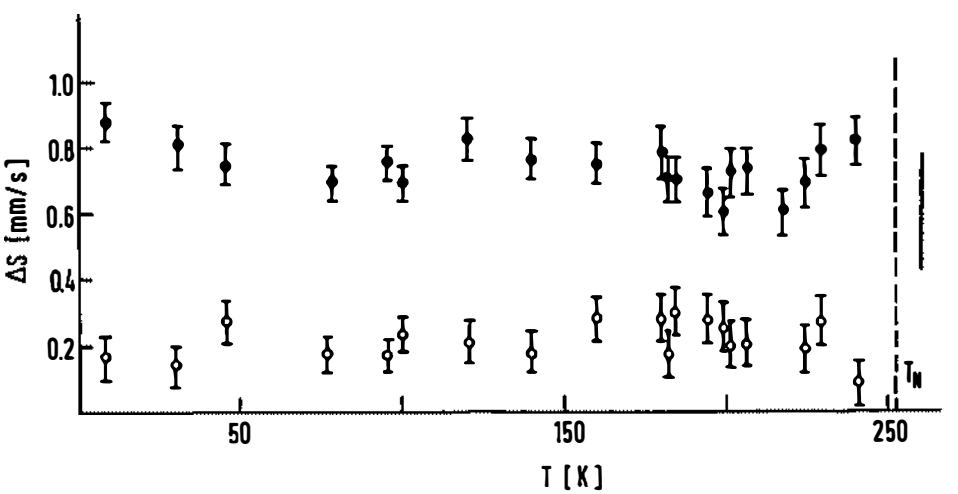

Fig. 5. Temperature dependence of the quadrupole splitting parameter ΔS for the octahedral and tetrahedral iron sites in $Bi_2Fe_4O_9$.

Above transition temperature the separation of the two quadrupole doublets represents the full value of the quadrupole splitting for octahedral and tetrahedral iron sites

$$\Delta E_Q = \frac{1}{2} eV_{zz} (1 - \gamma_\infty) Q \left(1 + \frac{\eta^2}{3}\right)^{1/2}, \tag{2}$$

where e is protonic charge, V_{zz} the largest component of the diagonalized EFG, $\eta = \frac{V_{xx} - V_{yy}}{V_{zz}}$ parameter of asymmetry and $\gamma_\infty = -9.14$ Steinheimer factor for iron[10].

At temperature $T = 320$ K the obtained values for the quadrupole splitting ΔE and isomer shift δ are

$$\Delta E_{Q_{tet}} = 0{,}96 \pm 0.02 \text{ mm/s}, \quad \delta_{tet} = 0.28 \pm 0.02 \text{ mm/s},$$
$$\Delta E_{Q_{oct}} = 0.40 \pm 0.02 \text{ mm/s}, \quad \delta_{ocr} = 0.39 \pm 0.02 \text{ mm/s}.$$

The results agree with those of Bokov et al[3] and Kostiner et al.[7]

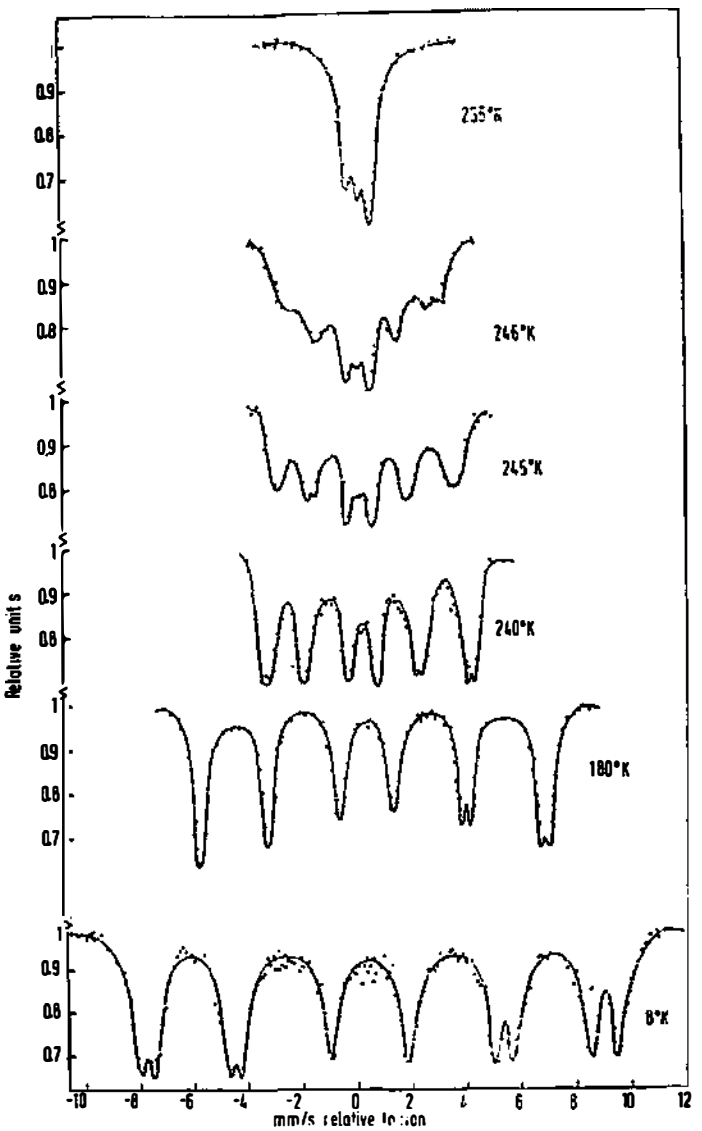

Fig. 6. Mössbauer spectra of $Bi_2Fe_4O_9$ at various temperatures taken with the source of ^{57}Co in Pd.

The difference in isomer shift at the octahedral and tetrahedral sites is relatively constant: $\delta_{oct} - \delta_{tet} = 0.12 \pm 0.02$ mm/s.

From the isomer shift systematics of Walker et al.[11], the partial covalency of about 20% is estimated in Fe-O bonding for the tetrahedral site. The temperature coefficients

$$\frac{1}{E}\left(\frac{\beta E}{\beta T}\right)_{oct} = 2.42 \cdot 10^{-15}/\mathrm{K} \text{ and } \frac{1}{E}\left(\frac{\beta E}{\beta T}\right)_{tet} = 2.25 \cdot 10^{-15}/\mathrm{K}$$

are in accordance with the results given for the garnets.

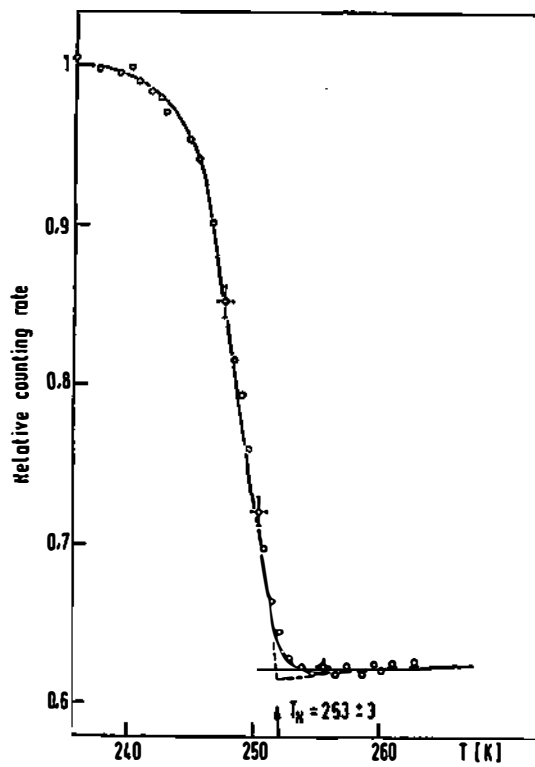

Fig. 7. Relative transmission at zero velocity as a function of absorber temperature.

The observed quadrupole splittings reflect the contribution of surrounding ions to the EFG as Fe^{3+} ions are spherically symmetric S state ions. Therefore the point charge lattice sum calculation of the EFG were evaluated for Fe^{3+} ions in octahedral and tetrahedral site separately using the De Wette Schacher[12] plane-wise method for which the computer program developed by Dickman[13]. Using X ray data of Niizeki for $Bi_2Fe_4O_9$, such calculation, which includes all charges in the lattice except the ion in question, yields following total EFG tensors for both iron sites

$$V_{ij}^{oct}(\mathrm{Fe}) = F \begin{array}{c} \begin{matrix} x & y & z \end{matrix} \\ \begin{bmatrix} 129.11 & 95.64 & 0.0 \\ 95.64 & -58.21 & 0.0 \\ 0.0 & 0.0 & 70.91 \end{bmatrix} \end{array},$$

$$F = \frac{10^{-3}\, e\,(1 - \gamma_\infty)}{4\pi\,\varepsilon_0}\,(A^0)^{-3} = 1.46 \cdot 10^{15}\ \mathrm{V/cm^2},$$

$$V_{ij}^{\mathrm{tet}}\,(\mathrm{Fe}) = F \begin{bmatrix} -76.42 & -\ 9.69 & -\ 2.44 \\ -\ 9.69 & -115.88 & -\ 3.99 \\ -12.44 & -\ 3.99 & 192.32 \end{bmatrix},$$

where x, y, z axes are chosen paralel to the crystallographic a, b, c axes and each iron and bismuth ion is represented by an equivalent charge $+3e$ and oxygen ion by $-2e$. These tensors were diagonalized in a principal axis system and specified by the diagonal elements V_{xx}, V_{yy}, V_{zz}. The largest eigenvalue V_{zz} is given in Table 1 together with its orientation relative to crystal axis and the parameter of asymmetry.

Table 1

$Bi_2Fe_4O_9$	$V_{zz} \cdot 10^{17}$ V/cm^2	η	orientation of V_{zz}
Fe^{3+}_{oct}	+2.47	0.16	in ab plane at angle 22.8 to a axis
Fe^{3+}_{tet}	+2.87	0.27	paralel to C within 2.7°

The largest axis of the field gradient V_{zz} for the tetrahedral iron site and the smallest axis V_{xx} of the octahedral iron site lie paralel to the crystal axis c in agreement with the point symmetry requirements.

Inserting the measured values for the quadrupole splitting ΔE and the calculated component V_{zz} and parameter of asymetry η into Equ. 2, we obtain the quadrupole moment of the first excited state of iron as $Q = 0.16 \cdot 10^{-24}$ cm^2 for the octahedral and $0.33 \cdot 10^{-24}$ cm^2 for the tetrahedral site. The values are estimated to be to 20% reliable. Considering the approximation made by assuming point charge lattice and neglecting other effects as for instance induced dipole moment on O^{2-} and the covalency, agreement with the values obtained by Bancroft[14]) and Sengupta[15]) is satisfactory for octahedral iron sites in $Bi_2Fe_4O_9$.

Acknovledgement

The autors are indebted to Mr. F. Dacar for preparation of the computer programes.

References

1) N. Niizeki and M. Wachi Z. Kristalogr. **127** (1968) 173;
2) A. G. Tutov I. E. Milnikova N. N. Parfenova, V. A. Bokov and S. A. Kižaev, Fiz. Tvred. Tela, **6** (1964) 1240;
3) V. A. Bokov, S. I. Jušik, G. V. Popov, N. N. Parfenova and A. G. Tutov, Fiz. Tverd. Tela **13** (1971) 1950;
4) V. A. Bokov, G. V. Norikov, V. A. Trhtanov and S. I. Jušuk, Fiz. Tverd. Tela, **11** (1969) 2871;
5) V. A. Bokov, A. S. Kamzin and G. Ja. Karapetjan, Fiz. Tverd. Tela, **14** (1972) 2495;
6) G. D. Achenbach, W. J. James and J. Gerson, J. Am. Ceram, Soc.. **50** (1967 437;
7) E. Kostiner and G. L. Shoemaker, Jour. Sol. St. Chem. **3** (1971) 186;
8) J. J. Van Loef, Physica **32** (1966) 2102;
9) E. Callen and H. B. Callen, J. App. Phys. **36** (1965) 1140;
10) R. M. Sternheimer, Phys. Rev. **130** (1963) 1423;
11) L. R. Walker, G. K. Wertheim and V. Jaccarino, Phys. Rev. Lett. **6** (1961) 98;
12) F. W. De Wette and G. E. Schacher, Phys. Rev. **137** (1965) A92;
13) D. B. Dickmann, Thesis, U. S. Noval Postgraduate School, Monterey, (1966);
14) G. M. B₂ncroft, Chem. Phys. Lett. **10** (1971) 449;
15) D. Sengupta, J. O. Artman nad G. A. Sawatzky, Phys. Rev. **B4** (1971) 1484.

RAZISKOVANJE $Bi_2Fe_4O_9$ Z MÖSSBAUERJEVIM EFEKTOM

D. HANŽEL i A. MOLJK

Institut »Jožef Stefan«, Ljubljana i *Fakultet za naravoslovje in tehnologijo, Ljubljana*

Vsebina

Antiferomagnetni $Bi_2Fe_4O_9$ je bil raziskovan z Mössbauerjevo spektroskopijo v temperaturnem področju od 8 do 550 K. Določena je bila temperatura prehoda $T_N = 253 \pm 3$ K in ekstrapolirana vrednost efektivnega magnetnega polja pri absolutni ničli za oktaedrsko železo 535 $\pm$ 5 KG in za tetraedrsko železo 485 $\pm$ 5 KG. Temperaturna odvisnost podmrežne magnetizacije je bila primerjana z Brillouinovo funkcijo za $S = 5/2$. V kritičnem področju $0.76 < T/T_N < 0.97$, je podmrežna magnetizacija podana z izrazom $M(T) = M(O)\, D\,(1 - T/T_N)$, kjer je $\beta_{oct} = 0.29$ in $\beta_{tet} = 0.31$.

Iz kvadrupolne cepitve v antiferomagnetnem področju in iz gradienta električnega polja, računanega po modelu točkastih nabojev, dobimo za kvadrupolni moment železovega jedra v prvem vzbujenem stanju vrednost $Q = 16 \pm 0.03$ b.