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Spin-Order and Magnetic Properties of $BaZn_2Fe_{16}O_{27}$ (Zn_2-W) Hexagonal Ferrite

G. Albanese, M. Carbucicchio
Istituto di Fisica dell'Università, Parma, Italy

G. Asti
Laboratorio MASPEC del CNR Parma, Italy

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Abstract. Mössbauer and magnetic measurements have been carried out both on single crystals and polycrystalline samples of $BaZn_2Fe_{16}O_{27}$(Zn_2-W) hexagonal ferrite. The saturation magnetization at 0 K and at room temperature turns out to be very high, that is, 123 and 79 Gauss · cm^3/g, respectively. The results have been interpreted by assuming a local reversal or a weakening of the Fe^{3+} magnetic moments due to the perturbing action of Zn^{2+} ions. The magnetic anisotropy is confirmed to be uniaxial with an anisotropy field at room temperature of 12.500 Oe.

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The so-called W-type hexagonal ferrite whose unit formula is $BaMn_2Fe_{16}O_{27}$ (Me_2-W; Me=Mn, Co, Zn, ect.) has a crystalline structure closely related to that of $BaFe_{12}O_{19}$ (M-type ferrite). As is shown in Figure 1, the unit cell is built up by the superposition of two spinell blocks (S-block) and a block containing Ba ions (R-block). The cations occupy seven different sublattices. In Table 1, the number of ions and the coordination of the different cation sublattices of the W-ferrite are reported. The spin orientation according to the generally accepted collinear model [1] is also indicated. In order to make the comparison with M-type structure easier we have also reported in the first column a nomenclature of the sublattices. This is a natural extension of that of M-type structure and takes more account of the magnetic behaviour of the cations in the various lattice sites. This magnetic classification has been employed for Mg_2-W compounds [2] and turns out to be consistent with the hyperfine fields actually observed. On the other hand, this point of view is justified by the assumption that the magnetic behaviour of a cation is determined mainly by the configuration of the nearest neighbors cations bounded by superexchange interactions.

In principle, the presence of divalent cations in the W-structure as compared to the M-structure, allows a greater possibility of changing the magnetic properties by a suitable choice of the cation species. In particular, the specific magnetic moment can be greatly increased by the presence of divalent or trivalent non-magnetic ions in the tetrahedral sites, of which there are a relatively large number in this structure. Due to these reasons, the W-ferrites appear as promising

Table 1. Number of ions, coordination and spin orientation for the various cation sublattices of W-type hexagonal ferrite

Magnetic sublattice	Sub-lattice	Coordination	Number of ions per formula unit	Block	Spin
K	$12K$	octahedral	6	R–S	up
f_{IV}	$4e$	tetrahedral	2	S	down
	$4f_{IV}$	tetrahedral	2	S	down
f_{VI}	$4f_{VI}$	octahedral	2	R	down
a	$6g$	octahedral	3	S–S	up
	$4f$	octahedral	2	S	up
b	$2d$	hexahedral	1	R	up

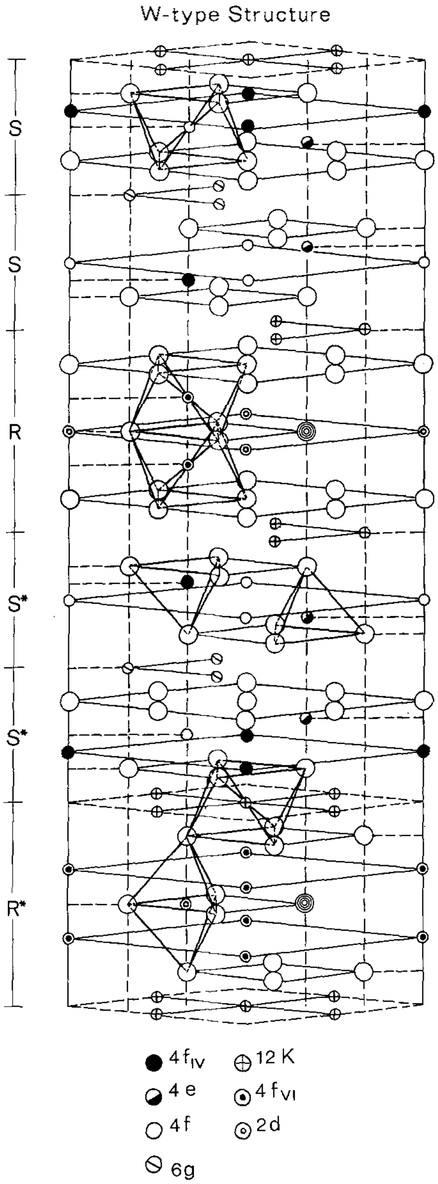

Fig. 1. Unit cell of the $BaMe_2Fe_{16}O_{27}$(Me−W) ferrite. The anions of O^{2-} (large empty circles), the divalent barium cations Ba^{2+} (○), the metallic ions in the sublattices $4f_{IV}$ (○); $4e$ (∅), $4f$ (○), $6g$ (∅), $12K$ (⊕), $4f_{VI}$ (○), and $2d$ (○) are indicated. The coordination figures of the metallic ions in the different lattice sites are shown

materials for technological application in the fields of permanent magnets and microwave devices.

Unfortunately, the lack of reliable experimental data in the literature does not allow a detailed analysis of their intrinsic properties on a microscopic scale. For this reason, we have started a systematic analysis of some important W-compounds. Some results relative to Mg_2-W ferrite have been reported in a previous paper [2]. In the present work, we report and discuss the results obtained by magnetic and Mössbauer [3] measurements on $BaZn_2Fe_{16}O_{27}$ (Zn_2-W) compounds. As is known, this is a case where a divalent non-magnetic ion (the Zn^{2+} ion) having a marked preference for tetrahedral coordination is expected to lead to a high saturation magnetization.

In fact, by assuming the basic collinear magnetic order for the W-compound, as indicated in Table 1, one expects for Zn_2-W at 0 K a magnetic moment per formula unit in Bohr magnetons (μ_B)

$$n_B = 12 \times 5\,\mu_B - 4 \times 5\,\mu_B = 40\,\mu_B\,.$$

Usually in the literature [4] the saturation magnetization per formula unit is calculated from the formula

$$(n_B)_W = (n_B)_M + 2(n_B)_S\,, \tag{1}$$

where $(n_B)_M$ and $(n_B)_S$ denote the corresponding values for M and S structures.

This formula is based on the way the W-structure is built up and gives for Zn_2-W a value of $(n_B)_W = 20\,\mu_B$. This discrepancy with the value calculated on the basis of the magnetic order may be ascribed to oversimplification in the assumptions which lead to (1). It takes no account of the fact that the divalent cations are distributed with the same probability in both the adiacent S-blocks of W-structure. For this reason, we cannot assign the value of $0 \cdot \mu_B$ to the contribution of one spinel block. It is already known that in the mixed spinel ferrites containing Zn the magnetic moment is maximum when the Zn concentration in the A-sites is about 50%. In fact, we obtain for the magnetic moment of Zn_2-W at 0 K an experimental value of $n_B = 35\,\mu_B$, which is well above the value of $20\,\mu_B$ according to (1).

In what follows we discuss our magnetic and Mössbauer results in terms of a statistical model which assumes that part of the Fe ions located in octahedral sites near Zn ions point their spin opposite to the magnetization of their sublattice.

1. Experimental Procedure

Mössbauer resonant absorption spectra of the $Fe^{57}-14.4$ KeV γ-radiation and magnetization measurements have been carried out on single crystals of $BaZn_2Fe_{16}O_{27}$ (Zn_2-W) ferrite. The single crystal absorber for Mössbauer measurements has been prepared by cleaving the selected single crystals along the basal plane. The obtained plates were reduced to $20 \div 30\,\mu m$ thickness and subsequently displayed on a mylar foil to form a mosaic with an area of 1 cm^2. Some Mössbauer spectra have been measured for polycrystalline absorbers which are prepared by grinding the smallest crystals. The Mössbauer measurements were performed by using a 10 mCi Co^{57} diffused in Cr matrix and a driving system at constant acceleration assocciated with a multichannel analyzer working in a multi-scaler time mode. The spectra were measured with the source at room temperature, while the absorbers were maintained at various temperatures ranging from 78 to 800 K. In some cases, the Mössbauer absorbers were placed in a 25 KOe external magnetic field perpendicular to the γ-ray direction.

The magnetization measurements for the single crystal samples were performed in the temperature range of 78–720 K by utilizing a vibrating sample magnetometer equipped with cryostat and oven assembly.

Particular care was devoted to the examination of the homogeneity, chemical composition and crystal structure of the samples used in this work[1]. For comparison, some measurements have been performed also on polycrystalline samples[2] prepared by the conventional grinding of the component oxides and solid-state reaction. The homogeneity of the samples has been checked by accurate Mössbauer and magnetization measurements in the neighborhood of the Curie temperature. The chemical analysis confirms that deviations from stoichiometry are negligible. All the samples we have used show the same pattern in the Mössbauer absorption spectra and the same values both for saturation magnetization and anisotropy field. Similar analysis carried out on single crystal samples of different origin have shown that the presence of an extraneous phase (probably $ZnFe_2O_4$) is very likely in this type of compound. The presence of this phase can be easily ascertained by the appearance of central paramagnetic peaks in the room temperature (R.T.) Mössbauer spectra.

2. Experimental Results

2.1. Mössbauer Measurements

The Mössbauer absorption spectrum of the Fe^{57} 14.4 KeV γ-rays for polycrystalline Zn_2-W samples at room temperature (R.T.) is shown in Figure 2. As indicated in the same figure, the spectrum can be interpreted as the superposition of five Zeeman sextets. The sextet V is denoted by a dotted line since the corresponding peaks, due to their low intensity, are difficult to detect. The interpretation of the spectrum was performed on the light of our previous study of Mg_2-W compounds [2]. It is evident from the R.T. spectrum that the sublattice magnetizations in the case of Zn_2-W are markedly different from those of Mg_2-W. In fact, in the case of the Mg_2-W compound, the sublattice K gives rise to very distinct peaks with a relative intensity proportional to its ion population. On the contrary, the relative line intensities in the spectra of Zn_2-W compound clearly show that the sextet I results not only from the contributions of K sublattice but also from iron ions located in other sublattices.

A spectrum was measured at room temperature with the absorber in an external magnetic field of 25 KOe perpendicular to the γ-rays direction. By comparing the hyperfine magnetic fields relative to the observed sextets both in the presence and in the absence of the external magnetic field we have established the spin orientation of the sextets.

The spectrum measured for the single crystal absorber at room temperature with the γ-rays direction parallel to the c-axis of the crystal is shown in Figure 3. The absence in this spectrum of the lines corresponding to $\Delta m = 0$ transitions is in agreement, within the experimental uncertainty, with the collinear uniaxial magnetic order of the Zn_2-W ferrite, as results from neutron diffraction data [5]. Moreover, the relative line intensities in the spectrum for the single crystal confirm that the sextet I arises from the contribution of several sublattices in addition to that of K-sublattice.

The correspondence between the sextets and the iron sublattices is indicated in the caption of Figure 2. It has been established by taking into account the spin orientation relative to the various sextets, the proportionality between the intensity of the sextets and the sublattice population, as well as the analogy with the M-type compounds previously studied [6].

In Figure 4, the temperature dependence of the hyperfine magnetic fields relative to the observed sextets is reported. The spectra measured at temperatures above the Curie temperature (T_c) consist in a paramagnetic doublet with a line separation $\Delta = 0.38$ mm/s (Fig. 5).

By measuring the temperature dependence of the line width we obtained for Zn_2-W ferrite a Curie temperature $T_c = 375 \pm 5°$ C.

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[1] Supplied by Harshaw Chem. Co.

[2] Kindly supplied by G. Sloccari of the Istituto di Chimica Applicata, Facoltà di Ingegneria, Università di Trieste.

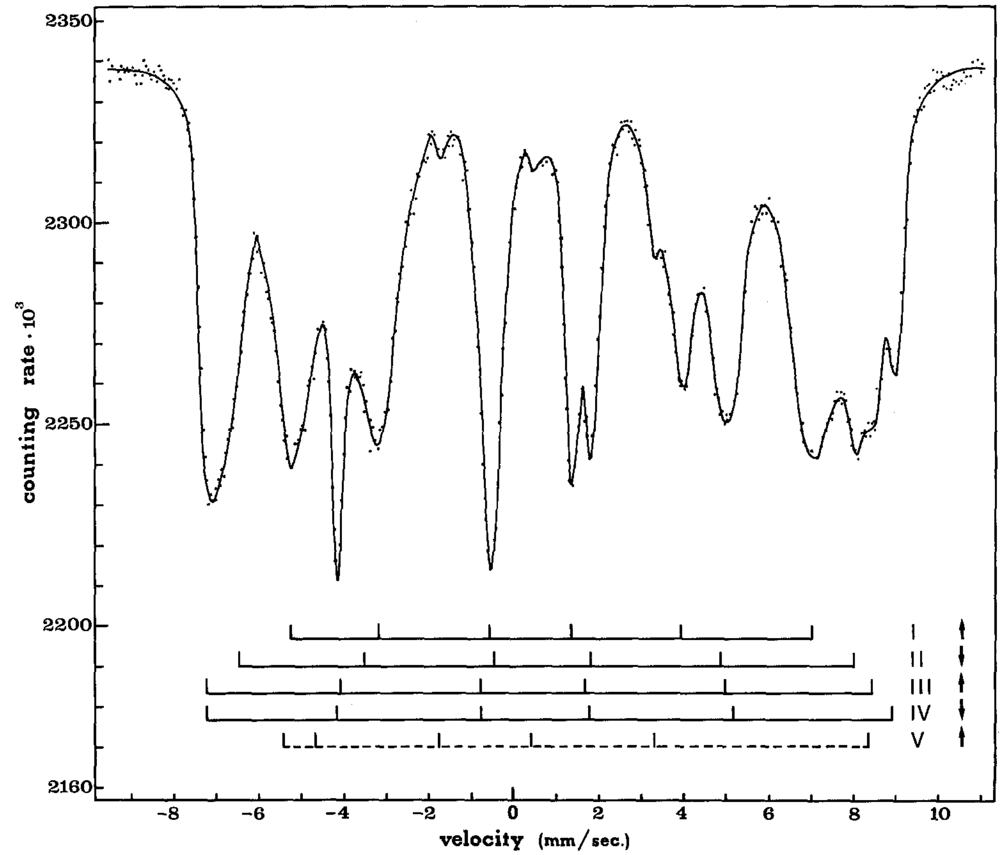

Fig. 2. Mössbauer spectrum of polycrystalline Zn_2-W compound at $T = 300$ K. (I: sublattice K and a part of sublattice "a", II: sublattice f_{IV}, III: the remanent part of sublattice a, IV: sublattice f_{VI}, V: sublattice "b"). The spin orientation of the iron sublattices contributing to the various sextets is indicated by arrows

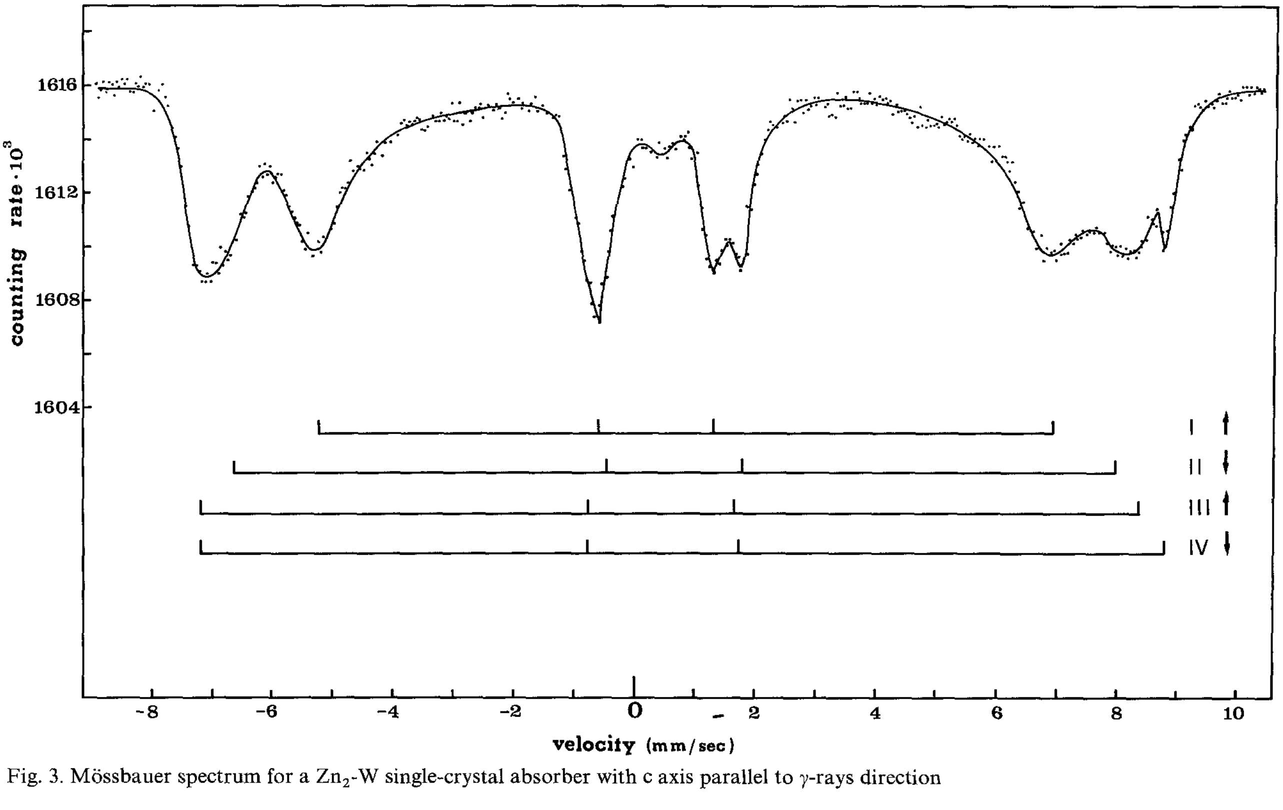

Fig. 3. Mössbauer spectrum for a Zn_2-W single-crystal absorber with c axis parallel to γ-rays direction

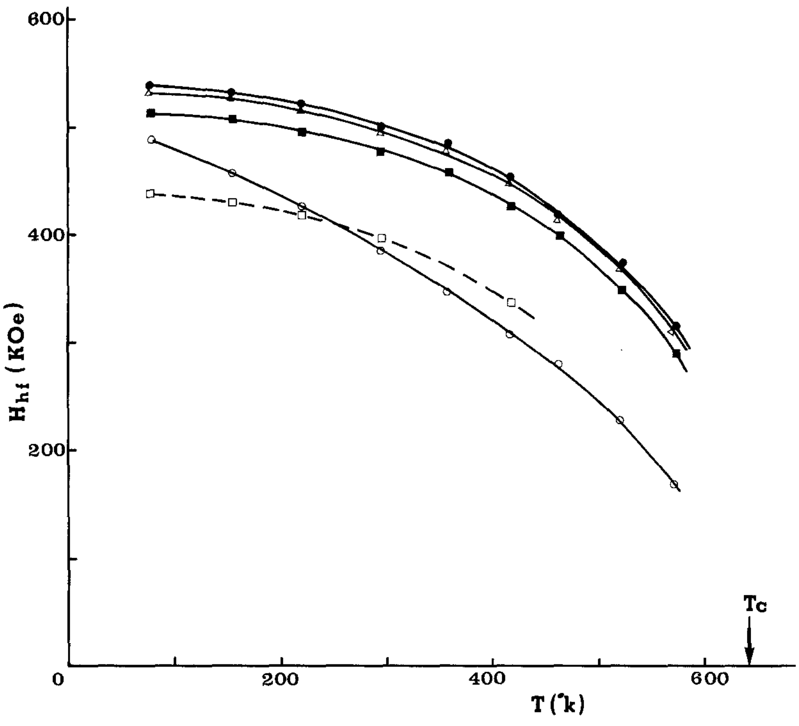

Fig. 4. Hyperfine magnetic fields at the Fe^{57} nuclei versus temperature relative to the various sextets observed in Mössbauer spectra of Zn_2-W compound. The open circles, the full squares, the triangles, the full circles and the open squares refers to sextets I, II, III, IV, V, respectively

2.2. *Magnetic Measurements*

Magnetic measurements in the temperature range of 78–720 K have been performed on single crystal samples both in the easy and the hard direction with an external field of up to 20 KOe.

From the obtained graphs $M(H)$, we have deduced the specific magnetic moment $\sigma(T)$ and the anisotropy field $H_A(T)$ as functions of the temperature. The obtained plots are reported in Figure 6 together with the anisotrpy constant $K_1 = H_A Ms/2$.

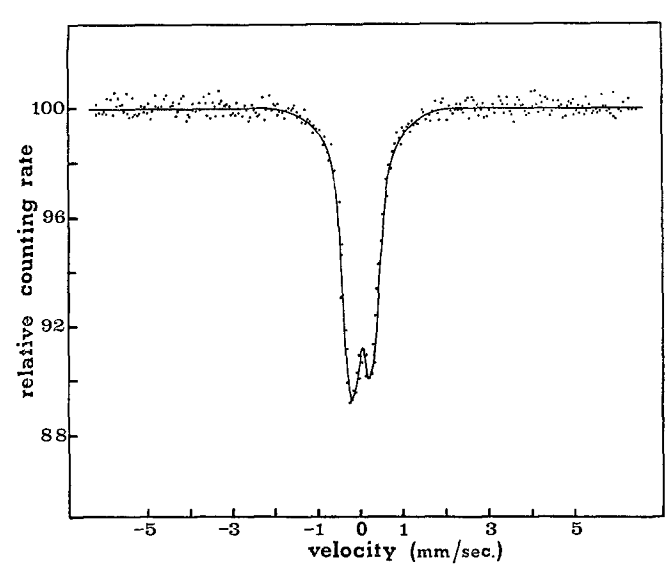

Fig. 5. Mössbauer spectrum for Zn_2-W compound at $T > T_c$

The Curie temperature turns out to be $T_c = 380+5°$ C which is in agreement with the value deduced by Mössbauer experiments.

In the entire temperature range the crystal display uniaxial anisotropy.

The saturation value of σ at 0 K has been determined by extrapolation and turns out to be $\sigma_0 = 123$ Gauss · cm^3/g which corresponds to a number of Bohr magnetons (μ_B) per unit formula $n_B = 35\,\mu_B$. Savage and Tauber [7] report for the Zn_2-W ferrite a value of $\sigma_0 = 134$ Gauss · cm^3/g and a more rapid decrease of σ with increasing temperature. Indeed they give a Curie temperature of about 60° C below our value.

It is worth noting that the value at room temperature $\sigma_{R.T.} = 79$ Gauss · cm^3/g measured at 20 KOe is substantially higher than that of any other hexagonal ferrite. It is well above the value of 70 Gauss · cm^3/g, which we have measured for a single crystal of $BaFe_{12}O_{19}$.

For this reason, despite the anisotropy lower than that of $BaFe_{12}O_{19}$, Zn_2-W seems to be of interest for special applications as permanent magnet material.

We have also carried out magnetic measurements on polycrystalline sintered samples prepared by conventional ceramic technique. The values we have found

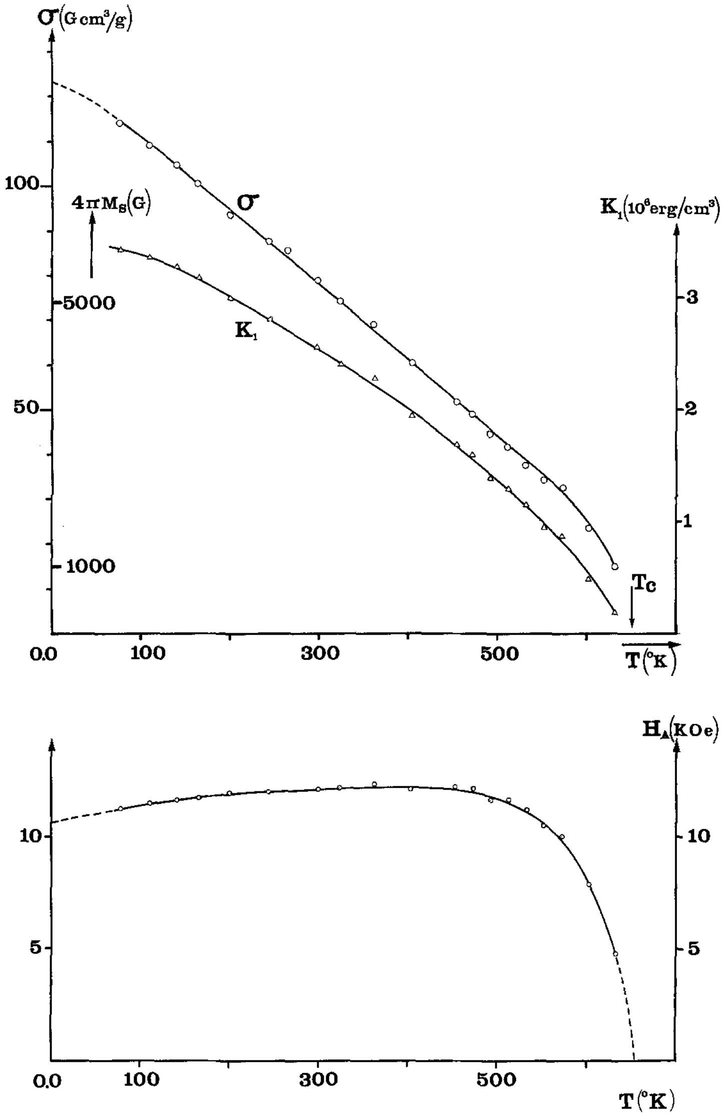

Fig. 6. Temperature dependence of saturation magnetization σ, of magnetic anisotropy field H_A, and of the first anisotropy constant K_1

confirm both the high σ observed and the magnitude of the anisotropy field.

For these measurements we have employed the singular point detection technique [8] both for the measurement of H_A and the correct evaluation of the saturation magnetization.

The value of the specific magnetic moment we have found in Zn_2-W ferrite both at low temperature ($\sigma_0 - 123$ Gauss · cm³/g) and at room temperature ($\sigma_{R.T.} = 79$ Gauss · cm³/g) is much higher than the value reported by some authors for the same compound ($\sigma_0 = 93$ Gauss · cm³/g, $\sigma_{R.T.} = 64$ Gauss · cm³/g) [1, 9]. We think that the presence of extraneous phases in the samples used by other authors is the main origin for such a discrepancy. Indeed, some measurements carried out by us on inhomogeneous crystals, that is, crystals containing as extraneous phase $ZnFe_2O_4$ ferrite, give values of σ_0 and $\sigma_{R.T.}$ which are very close to those reported in the literature. We claim that it is difficult to distinguish the presence of the extra phase $ZnFe_2O_4$ merely by magnetic or röntgenographic analysis in these kinds of compounds. On the contrary, in the Mössbauer spectra the paramagnetic $ZnFe_2O_4$ phase gives rise to a central doublet clearly distinguishable from the main pattern which is due to the Zn_2-W compound.

3. Discussion

Although the value of the saturation magnetization we have found in Zn_2-W is relatively high, it turns out to be lower than the upper theoretical limit of 40 μ_B. This discrepancy can be explained taking into account the weakening of tetrahedral-octahedral superexchange interactions due to the high concentration of Zn^{2+} ions in tetrahedral sublattices. The local weakening of the superexchange interactions in ferrimagnetic oxides can give rise to a random canting of the magnetic moments [10, 11] or to a local spin reversal [12, 13].

In the case of Zn_2-W ferrite the only sublattice which can suffer canting is the sublattice "a". Indeed the other spin up sublattice (12*K*) which interacts with tetrahedral ions is strongly coupled with the $4f_{VI}$. In order to justify the observed magnetization of 35 μ_B the average canting angle for the sublattice "a" must assume a value of 37°. Up to now all the available experimental data seem to exclude angles of such magnitude. For this reason we carry out in the following an analysis of our results in terms of the local spin reversal model.

In Zn_2-W ferrite the Zn^{2+} ions occupy a fraction of 50% of the available tetrahedral sites. Depending on the way these ions are distributed inside these sublattices, one can have different situations as far as the local magnetic order is concerned. If an iron ion located in an octahedral site (in our case the "a" sublattice) has a number $K<2$ of Fe^{3+} ions in tetrahedral sites as nearest neighbours, its magnetic moment can be reversed due to the action of octahedral-octahedral interactions. Instead, in the case $K \geqq 2$, the magnetic moment preserves its direction but displays lower values [12].

Let us give the expression for the probability *P* that an Fe^{3+} ion in the sublattice "a" sees less than two tetrahedral nearest neighbour Fe^{3+} ions (viz. the case $K<2$), supposing a statistical distribution of Zn^{2+} in the tetrahedral sublattices 4*e* and $4f_{IV}$.

Taking into account that in the W-structure we have two non-equivalent tetrahedral sublattices (4*e* and $4f_{IV}$), we must consider the possibility of a certain preference of Fe^{3+} ions for one of them. Hence denoting by *p* the degree of preference of Fe^{3+} ions for 4*e* sites, we find expression

$$P=\tfrac{1}{5}p(1-p)^2\left[-5p^3+14p^2-9p+6\right], \qquad (2)$$

which is plotted in Figure 7. The presence of a maximum in this plot implies the existence of a lower limit for σ equal to 33.5 μ_B. The upper limit for σ, corresponding to $p=0$ or $p=1$, is 40 μ_B i.e. the maximum value allowed for Zn_2-W ferrite with a strict collinear order.

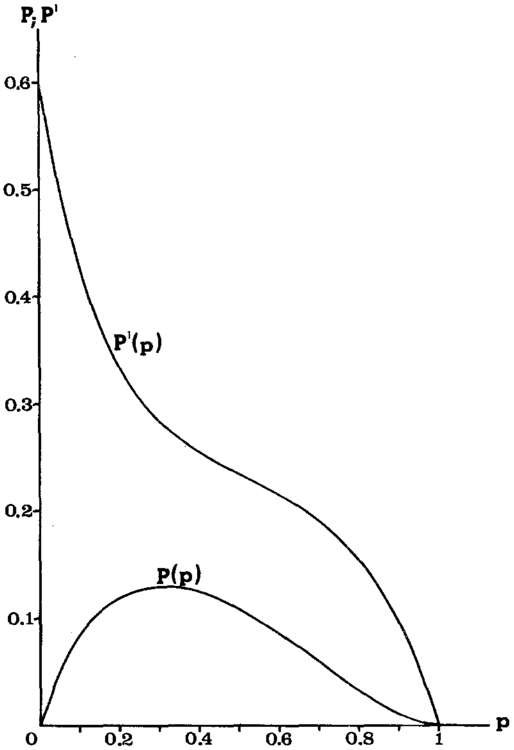

Fig. 7. Dependence of functions *P* and *P'* on the degree of preference, *p*, of Zn^{2+} ions for 4*e* sublattice. *P* and *P'* denote the probabilities that an Fe^{3+} ion in "a" sublattice sees less than two or two tetrahedral nearest-neighbors Fe^{3+} ions, respectively

From the value of saturation magnetization we have found, which correspond to a number of Bohr magnetons $n_B=35.0\pm0.5$, we can deduce the number of Fe^{3+} ions in "a" sublattice per formula unit having reversed spin. This number turns out to be about 0.5, to which corresponds a value of $P=0.1$. From the graph in Figure 7, we can see that $p=0.5$ corresponds to this value. In practice that means a non-preferential distribution of Zn^{2+} ions between the two tetrahedral sublattices 4*e* and $4f_{IV}$. The higher value of σ_0 reported in [7] could be interpreted as due to a more ordered distribution of Zn^{2+} ions in tetrahedral sites as a consequence of a different thermal treatment of the samples.

As we pointed out in Section 2.1, the number of Fe^{3+} ions giving rise to sextet I is greater than the amount of Fe^{3+} ions both in *K* and *b* sublattices. This result comes from the analysis of the areas submitted by various sextets in Mössbauer spectra. This means that there are other ions whose magnetic moment undertake the same rapid decrease with increasing temperature as the Fe^{3+} ions in K sublattice. This is a further consequence of the perturbing action of Zn^{2+} ions, besides the above mentioned local spin reversal.

In the frame of our model, this effect occurs when $K=2$; that is, when the Fe^{3+} ions in "a" sublattice see two tetrahedral Fe^{3+} ions as nearest neighbors.

The probability for this surrounding is

$$P' = \tfrac{3}{5}(1-n)(-5p^3+15p^4-16p^3+10p^2-3p+1)\,, \quad (3)$$

which is also plotted in Figure 7. Equation (3), by assuming $p=0.5$ yields $P'=0.23$. Accordingly, the number of ions contributing to sextet I must be

$$n_1 = 6[K] + 1[b] + P' \cdot 5[a_{K=2}] = 8.15$$

and the number of remanent ions is

$$n_2 = 2[f_{\mathrm{IV}}] + 2[f_{\mathrm{VI}}] + (0.9-P')5[a_{K>2}] = 7.35\,.$$

The ratio turns out to be $n_1/n_2 = 1.11$, which is in agreement with the relative line intensities in Mössbauer spectra.

Regarding the magnetic anisotropy properties, we observe that Zn_2-W ferrite is characterized by a temperature dependence of the anisotropy field similar to that of $BaFe_{12}O_{19}$ which is nearly constant up to high temperatures.

The first anisotropy constant K_1 at low temperature turns out to be slight higher than expected if we take into account the corresponding value for $BaFe_{12}O_{19}$ and the relative dimensions of the elementary cells.

4. Conclusions

The saturation magnetization σ_0 of Zn_2-W ferrite turns out to be equal to 123 Gauss · cm^3/g; that is, 35 μ_B per formula unit. Thus, this is the highest value in comparison with other hexagonal ferrites.

The difference between the measured value of σ_0 and the value of 40 μ_B deducible from the collinear order generally assumed for W-structure is ascribed to local spin reversal inside the octahedral sublattice of the S block. This is caused by the weakening of tetrahedral-octahedral superexchange interactions due to the high concentration of Zn ions in tetrahedral sublattice. For another part of Fe^{3+} octahedral ions a further effect is observed as a remarkable decrease of their magnetic moment with increasing temperature.

References

1. W.H. von Aulock: *Handbook of Microwave Ferrite Materials* (Academic Press, New York 1965)
2. G. Albanese, G. Asti: IEEE Trans. *MAG*-**6**, 158 (1970)
3. U. Gonser (Editor): *Mössbauer Spectroscopy*, Topics Appl. Phys. **5** (Springer, Berlin, Heidelberg, New York 1975)
4. J. Smit, H.P. Wijn: *Ferrites* (Philips Tech. Library, Eindoven 1959)
5. R.A. Sizov, K.N. Zaitzev: Sov. Phys. JETP **39**, 175 (1974)
6. G. Albanese, M. Carbucicchio, A. Deriu: Phys. Stat. Sol. (a) **23**, 351 (1974)
7. R.O. Savage, A. Tauber: J. Am. Ceram. Soc. **47**, 13 (1964)
8. G. Asti, S. Rinaldi: J. Appl. Phys. **45**, 3600 (1974)
9. M.M. Shieber: *Experimental Magnetochemistry* (North Holland Pub., Amsterdam 1967)
10. S. Geller: J. Appl. Phys. **37**, 1408 (1966)
11. A. Sosencwaig: Can. J. Phys. **48**, 2857 (1970)
12. U. Konig: Int. J. Magnetism **3**, 63 (1972)
13. I. Nowik: Phys. Rev. **171**, 550 (1968)