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NEUTRON-DIFFRACTION STUDY OF THE MAGNETIC STRUCTURE OF HEXAGONAL FERRITES OF THE Co_{xW} SYSTEM

(Presented by Academician N. V. Belov on 20 IX 1965)

The system under investigation, described by the formula $BaCo_x^{2+}Fe_{2-x}^{2+}Fe_{16}^{3+}O_{27}$, belongs to the large class of complex ferrimagnetic oxides having hexagonal or rhombohedral symmetry. The structural type of the ferrites of this system is denoted in the literature by the symbol W. The crystal structure of hexagonal W ferrites was studied in detail in Brown' s work ([1]). The complex structure of these compounds may be represented as an alternation, along an axis perpendicular to the hexagonal axis, of layers (blocks) of cubic and hexagonal packing. Each unit cell consists of two cubic (spinel) and two hexagonal blocks and contains two formula units. According to Brown and our data, the unit-cell dimensions are: $a = 5.88$ Å and $c = 32.8$ Å.

Proceeding from consideration of the dependence of the magnitude of the exchange interaction on the Me—O—Me distance, Gorter ([2]) proposed a scheme for the orientation of spins located in different crystallographic positions, satisfactorily explaining the macroscopic magnetic properties of Fe_2W ferrite.

A detailed study of the magnetic properties of ferrites of this system, carried out by T. M. Perekalina and A. V. Zalesskii ([3]), showed a displacement of the easy-magnetization axes from the c axis toward the basal plane, with the formation of cones of easy magnetization, whose aperture angle depends on the Co content and on temperature.

In order to determine the spin ordering in ferrites of the Co_{xW} system, we performed a neutronographic study using polycrystalline and single-crystal samples having compositions $x = 0$; 0.5; 1.0; 1.5 and 1.75. To prepare the samples, single crystals grown from solution in a melt were used. Chemical-analysis and X-ray diffractometry data for the grown single crystals showed the presence in them of a single W phase within the accuracy limits of both methods. The unit-cell dimensions and space group proved identical to those given in ([1]).

For the purpose of accurately taking extinction into account, the single-crystal samples were given (by mechanical treatment followed by etching) a regular spherical shape (diameter 5 mm). The polycrystalline samples were prepared by pressing into thin-walled aluminum cylinders, 15 mm in diameter and 30 mm high, powder obtained by mechanical grinding of single crystals and annealed to relieve stresses.

Neutron-diffraction patterns were recorded using the neutron diffractometer described in ([4]). The investigations were carried out in the temperature range from 77 to 770° K. To separate the nuclear contribution, measurements in a magnetic field of $\sim 20\,000$ oersted, parallel to the scattering vector ε, were used. In general terms, the neutron-diffraction pattern from polycrystalline samples is characterized by the presence of well-resolved basal reflections 004 and 006, a very strong reflection, predominantly of magnetic origin, formed by the triplet $(100 + 101 + 102)$, and by a number of other reflections.

weaker overlapping reflections $(104 + 008)$, $(108 + 0010)$, and $(110 + 109)$, of which the reflections 008 and 110 are of greatest interest.

Figure 1 shows the diffraction patterns of the compositions $Co_{1.75}W$ (a), Fe_2W (b), and a neutronogram of Fe_2W, taken in a magnetic field parallel to ε (c) ($T = 293^{\circ}$K). In the neutronogram of Fe_2W, reflections from planes parallel to the basal planes are due only to nuclear scattering, which indicates the probable arrangement of the spin magnetic moments perpendicular to the basal plane, i.e., along the c axis. Taking into account that the absolute value of the saturation magnetization and its temperature dependence for ferrite Fe_2W (5) agree well with Gorter' s scheme, we accepted its validity for this case. As for the neutronogram of $Co_{1.75}W$, the basal reflections 004 and 006 contain a considerable magnetic contribution. Its existence can be explained by a deviation of the spins from the c axis.

Assuming the preservation of the Gorter model of two "sublattices" with oppositely directed spins oriented along a new axis forming a certain angle α with the c axis, one can obtain correct values of the magnetic contributions to the diffraction pattern and of the absolute values of the saturation magnetization (5). Having adopted this scheme of magnetic ordering, we calculated the values of the angles α, based on the observed magnetic intensity of the 006 and 004 reflections, using the formula

$$I_{\text{magn}}^{\text{obs}} = K_{hkl} \sin^2 \alpha \, F_{hkl}^2,$$

where K_{hkl} is a quantity constant for a given reflection, including the instrumental constant, geometrical factors, the absorption factor, etc.; α is the angle between the c axis and the direction of the spins; F_{hkl} is the structure factor. The theoretical intensities of the remaining reflections were calculated using the obtained values of the angles α.

Fig. 1

Fig. 1

Figure 1: Fig. 1

Table 1 gives the calculated and measured values of the intensities of the magnetic reflections I and of the angle α at a temperature of 293°K for the compositions Fe_2W, $Co_{0.5}W$, $Co_{1.0}W$, $Co_{1.5}W$, and $Co_{1.75}W$. The Co^{2+} and Fe^{2+} ions were assigned the positions $12k$ and $z = 0.1499$. The form-factor values for Fe^{3+} were taken from (6), and for Fe^{2+} and Co^{2+} from (7). The temperature correction was introduced according to the data of work (1). The value $(\sigma/\sigma_0)^2$ was obtained from the magnetization curves (5). The values $\langle q^2 \rangle$ for powder neutronograms were calculated according to (8).

Establishing the general features of the model of spin ordering and determining the angle between the spin axes and the c axis is limited by the infor-

Table 1

Composition	T, °K	100+101 I_{calc}	100+101 I_{meas}	110+002 I_{calc}	110+002 I_{meas}	111+004 I_{calc}	111+004 I_{meas}	006 I_{meas}	Angle α, deg.*
Fe_2W	293	18230	17530	1270	1200	1880	1976	0	0
Fe_2W	77	22800	21920	1590	1520	2380	2210	0	0
$Co_{0.5}W$	293	17950	17050	1250	1160	1850	1960	0	0
$Co_{0.5}W$	77	22600	21760	1790	1730	2370	2246	403	13
$Co_{1.0}W$	293	17600	16930	1240	1360	1815	1720	0	0
$Co_{1.0}W$	77	17540	16480	2870	2630	1950	2030	3465	45
$Co_{1.5}W$	293	14240	13610	2000	1840	1490	1580	2120	39
$Co_{1.5}W$	77	17190	16360	2830	2980	1900	1776	3480	45
$Co_{1.75}W$	293	9640	9000	3140	2910	1110	1180	5310	90
$Co_{1.75}W$	77	12080	11660	4020	3800	1460	1300	6620	90

* Maximum error in the value of the angle is ±5°.

mation that could be obtained in the present case from analysis of neutron-diffraction patterns on polycrystalline samples. Additional information was obtained from observations of the temperature dependence of the intensity of magnetic reflections from single-crystal samples.

Figure 2 shows curves of the temperature dependence of the intensity of reflections 006 (a) and 110 (b), measured on single-crystal samples in the temperature interval from 77 to 770°K (the Curie temperature for all the compositions studied is 758 ± 5°K). It is evident from the figure that for each composition there are characteristic temperature intervals in which the spin rotates away from the c axis by an angle α (see Table 1), accompanied by an increase in the magnetic contribution to reflection 006. At the same time, in the same temperature

intervals the magnetic contribution to reflection 110 decreases. The decrease in intensity is the same for all six 110 reflections recorded when the sample is rotated about the c axis. The only explanation for this can be the transformation of a single-domain single crystal, for which $\alpha = 0$, into a multidomain one ($\alpha \neq 0$), with its own spin axis for each domain. A similar picture was observed ([9]) for hexagonal cobalt: here, when the spins were deflected from the c axis into the basal plane ($\alpha = 90°$), a magnetically uniaxial (single-domain) crystal split into domains whose spin axes form

Fig. 2

an angle of 120° with one another. Confirmation of the existence of an analogous mechanism of domain splitting in single crystals of Co_{xW} is provided by the detection, in samples of this system for $\alpha \geq 45°$, of six easy magnetization axes lying in the basal plane at an angle of 60° to one another ([3]).

Table 2

hkl	$Co_{0.5}W$	$Co_{0.5}W$	$Co_{1.0}W$	$Co_{1.0}W$	$Co_{1.5}W$	$Co_{1.5}W$	$Co_{1.75}W$	$Co_{1.75}W$
	a^*	b^*	a	b	a	b	a	b
006	1.9	1.95 ± 0.2	6.1	6.2 ± 0.4	1.37	1.40 ± 0.1	1.25	1.18 ± 0.05
110	1.06	1.04 ± 0.06	1.14	1.07 ± 0.06	1.11	1.12 ± 0.07	1.10	1.10 ± 0.07

* a –ratio $I^{-77°K}_{calc} E_p^{77°K} / I^{-293°K}_{calc} E_p^{-293°K}$; b –ratio $I^{-77°K}_{meas} / I^{-293°K}_{meas}$

In Table 2 the measured and calculated neutron-diffraction intensities for single crystals of Co_{xW} are compared for several reflections with the largest magnetic contribution. The value of E_p for all reflections was calculated analogously to ([10]). The expression for $\langle q^2 \rangle_{\text{single crystal}}$ was obtained by averaging over the angles η between the normal to the reflecting plane and the spin axes of the domains, whose projections onto the basal plane form an angle of 120° with one another (for the given case of the arrangement of spin axes, $\langle q^2 \rangle_{\text{single crystal}} = \langle q^2 \rangle_{\text{polycr}}$). The error in the intensity measurements did not exceed ±10%.

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Note: Figure translations are in progress. See original paper for figures.