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A NEUTRON DIFFRACTION STUDY OF THE STRUCTURE OF MAGNETOPLUMBITE

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Single crystals of $PbFe_{12}O_{19}$ have been studied at temperatures of 78 and 293°K, as well as single-crystal and polycrystalline $BaFe_{12}O_{19}$ and $SrFe_{12}O_{19}$ in the temperature region from 4.2 to 820°K. Corrections to the atomic coordinates of $BaFe_{12}O_{19}$ have been introduced. It has been established that at the temperatures studied the analogs of magnetoplumbite show axial collinear structures with ordered spins along the hexagonal axis in accordance with the scheme of Gorter. It has been determined that, from specimen to specimen and depending on the temperature, the mosaic block thickness and mosaic scatter vary within the limits $t \sim 0.001$-0.0025 cm and $\eta \sim 15$-$30''$.

Magnetic structures of a new type have been revealed in crystals of scandium-substituted magnetoplumbite [1, 2], and the study of a series of anomalies in these structures has required verification of the atomic coordinates and the determination of the parameters necessary for the calculation of neutron diffraction charts from single crystals. This work was carried out in the Institute of Nuclear Studies of the Polish Academy of Sciences (Swierk, Poland) on the "EWA" [EVA] reactor.

We investigated $BaFe_{12}O_{19}$, $SrFe_{12}O_{19}$, and $PbFe_{12}O_{19}$. Powdered specimens and single crystals of the Ba and Sr analogs of magnetoplumbite were investigated at 4.2, 78, 293, and 820°K, and single crystals of $PbFe_{12}O_{19}$ were investigated at 78 and 293°K. The results were processed on a "GIER" computer.

The investigation of the powders allowed refinement of the atomic coordinates and the magnetic structure model suggested earlier by Gorter [3] on the basis of analysis of magnetic properties as applied to the Kramers-Anderson indirect exchange theory [4, 5]. The atomic structure of magnetoplumbite (space group $P6_3/mmc$) was first studied by x-ray diffraction and described by Adelsköld in 1938 [6]. Later Braun [7] pointed out a series of inaccuracies in the coordinates, and Kay, referring to unpublished data of Braun, gave revised coordinates in a report [8]. The presence of the heavy lead atom in the structure makes the x-ray localization of oxygen atoms difficult. It was to be expected that neutron diffraction would introduce corrections into the coordinates of the latter.

Powder specimens were prepared by grinding single crystals grown by the method of crystallization from solution in a melt. The single crystals were tested for single-phase character by x-ray diffraction. The powder was placed in a cylindrical aluminum container of dimensions 15 × 40 mm. The unit cell parameters of the crystals studied, as determined by x-ray diffraction, are given in Table 1.

Analysis of intensities of the powder neutron diffraction patterns (the typical form of one of them is given in Fig. 1) showed that for $SrFe_{12}O_{19}$ better agreement of experimental and calculated structure amplitudes ($R = 0.05$-0.08) is observed for the coordinates taken from [6-8]. In the case of $BaFe_{12}O_{19}$, however, for all temperatures of study the best R factor was obtained for a change of the

TABLE 1

Composition	c, Å	a, Å
$BaFe_{12}O_{19}$	23.18	5.80
$SrFe_{12}O_{19}$	22.98	5.78
$PbFe_{12}O_{19}$	23.09	5.78

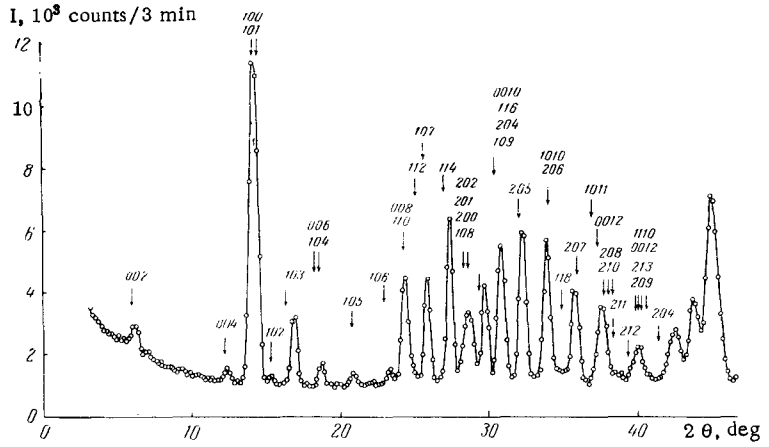

Fig. 1. Neutron diffraction pattern of $BaFe_{12}O_{19}$, $\lambda = 1.22$ Å, $T = 4.2$°K.

coordinates of the O_4 and O_5 oxygen atoms (positions $12k_1$ and $12k_2$). Changes in the coordinates of the other oxygen atoms and of the Fe_4 and Fe_5 atoms did not lead to noticeable improvement in agreement. In this case the coordinates were varied within the limits ± 0.0050 with respect to the values taken from [6-8] by the trial and error method. The atomic coordinates of the $BaFe_{12}O_{19}$ which we studied and the corresponding parameters of $PbFe_{12}O_{19}$ and $SrFe_{12}O_{19}$ from [6-8] are given in Table 2.

A list of R factors for the structure of $BaFe_{12}O_{19}$, determined from the powder neutron diffraction and depending on the temperature of the specimen, is given in Table 3.

During the calculation we accepted the magnetic model of Gorter, in which the spins of the iron atoms are located along the hexagonal axis of the crystal. The spins of the $4f_1$ and $4f_2$ iron sublattices are directed antiparallel with respect to the spins of the ions in positions 2a, 2b, and 12k.

TABLE 2

Atoms and their positions	Atomic coordinates			
	$PbFe_{12}O_{19}$, $SrFe_{12}O_{19}$ from [6-8]		$BaFe_{12}O_{19}$	
	x/a	z/c	x/a	z/c
Ba, Sr, Pb (2d)	2/3	1/4	2/3	1/4
Fe_1 (2a)	0	0	0	0
Fe_2 (2b)	0	1/4	0	1/4
Fe_3 ($4f_1$)	1/3	0.0271	1/3	0.0271
Fe_4 ($4f_2$)	1/3	0.1902	1/3	0.1902
Fe_5 (12k)	0.1667	—0.1083	0.1667	—0.1083
O_1 (4e)	0	0.1497	0	0.1497
O_2 (4f)	1/3	—0.0495	1/3	—0.0495
O_3 (6h)	0.1861	0.2501	0.1861	0.2500
O_4 ($12k_1$)	0.1667	0.0539	0.1620	0.0539
O_5 ($12k_2$)	0.5000	0.1490	0.5000	0.1480

TABLE 3

T, °K	R factors	
	from coordinates of [6-8]	from coordinates of this work
4.2	0.085	0.078
78	0.090	0.082
293	0.102	0.062
820	0.171	0.138

The neutron diffraction patterns did not have superstructure reflections or any other sort of anomaly, except for the powder diffraction pattern of $SrFe_{12}O_{19}$. In this case a noticeable increase in background was observed in the region of the (102)-(103) and (105)-(106) reflections. A special study of the 00l reflections from single crystals of this composition at 4.2°K did not reveal magnetic superstructure or noncollinearity of spin. The phenomenon mentioned above was attributed to the presence of a foreign phase which appears in noticeable amount only at liquid-helium temperature. Thus, it can be considered that, in the temperature region studied, the analogs of magnetoplumbite which were examined represent axial collinear structures from the magnetic point of view.

An attempt to introduce an average temperature correction into the calculated structure amplitudes did not result in substantial improvement of the divergence factor. In this case the thermal vibration constant B was varied from 0.2 to 2.0. This result may be caused by the small range of reflections investigated ($\sin\theta/\lambda \leq 0.25$ Å^{-1}).

Confidence in the atomic coordinates and in the distribution of the magnetic moments allowed us to carry out analyses of the neutron diffraction pat-

terns from single crystals of various thicknesses of these compounds and to determine the thicknesses t of the mosaic blocks and values of mosaic scatter η. It was established that, depending on temperature, the values of variation from specimen to specimen were within these limits: t = 0.001-0.0025 cm, η = 15-30".

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