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Fe^{2+} BEHAVIOUR IN La – SUBSTITUTED M – TYPE HEXAFERRITE[1]

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The charge compensation of electron deficiency of La^{3+} in comparison with Pb^{2+} takes place in La-substituted magnetoplumbite giving rise to Fe^{2+} ions in Fe^{3+} sublattices. The temperature dependence of electron mobility is studied in the temperature range of $5 \div 296$ K. The M-type hexagonal ferrite of the composition $Pb_{0.7}La_{0.3}Fe_{12}O_{19}$ was used in the powder form for Mössbauer experiments and in the single-crystalline form for conductivity measurements. The obtained results are in agreement with previous observations and allow to determine three temperature ranges with various charge transfer activation energies.

The hexagonal ferrites have attracted great interest due to the technological importance of their magnetic properties achieved by various substitutions. The crystal structure of the M-type hexagonal ferrites consists of a closely packed oxygen lattice partly substituted by large cations with five types of interstitials occupied by Fe^{3+} ions [1]. The Fe^{3+} sites denoted as 12k, $4f_2$ and 2a have octahedral, the $4f_1$ site has tetrahedral and the 2b position has a bipyramidal (two trigonal) symmetry, respectively. The doping by large La^{3+} cations is the cause of the extremely high value of magnetic anisotropy at low temperatures [2]. Previous investigations have proved that the charge compensation of the electron deficiency of La^{3+} in comparison with Pb^{2+} is realized in the magnetoplumbite lattice by the presence of divalent iron ions. Mössbauer study [3] indicated electron hopping within of the 2a cation sublattice in the partly La-substituted ferrite at room temperature, while the NMR experiment [4] showed the picture of immobile ferrous ions located at the 2a sites at liquid helium temperature. Here the temperature dependence of charge transfer dynamics is studied within of the temperature limits given above.

The single-crystalline sample with composition $Pb_{0.7}La_{0.3}Fe_{12}O_{19}$ was prepared by a flux method in the form of a platelet. Using a diamond saw and mechanical polishing the thickness of the platelet was diminished to approximately 50 μm. The angle between the normal to the platelet surface and the c-axis was less than 3° , as confirmed by X-ray

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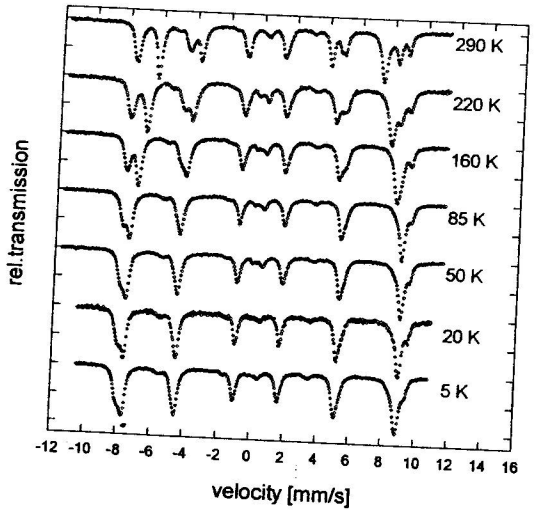

Fig.1: Transmission ^{57}Fe Mössbauer spectra of $Pb_{0.7}La_{0.3}Fe_{12}O_{19}$

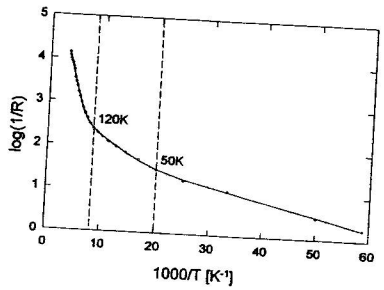

Fig.2: Temperature dependence of the electrical conductivity of $Pb_{0.7}La_{0.3}Fe_{12}O_{19}$ fitted with function $\sum_{i=1}^{3}[a_iT^{-1}\exp(b_iT^{-1})]$

diffraction. The powder sample of the same composition was obtained by milling of the single crystal. The single-crystalline sample was placed into a helium flow cryostat and its electrical conductivity was measured by four-point method in the temperature range of $17 \div 289$ K. Because of poorly defined geometry, only the temperature dependence was determined instead of the absolute value of conductivity. The powder sample was utilized for measuring a series of transmission ^{57}Fe Mössbauer spectra at temperatures of 290, 220, 160, 85, 50, 20 and 5 K - see Fig.1. The spectra were recorded into 500 channels (after folding) on a conventional spectrometer working in a constant acceleration mode. The calibration of velocity scale and zero isomer shift was provided by 8μm α-iron foil.

The measured shape of the temperature dependence of the conductivity is semiconductor-

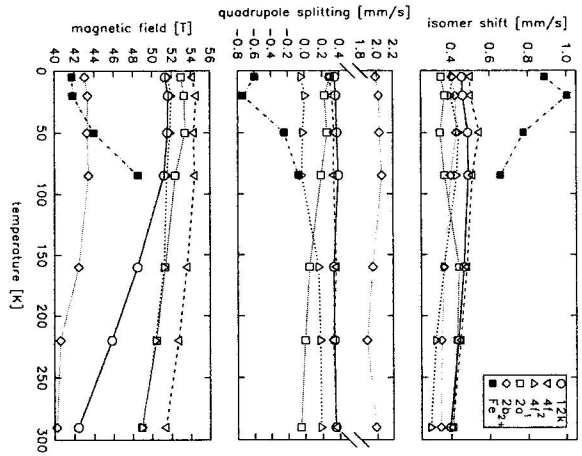

Fig.3: Temperature dependence of the hyperfine parameters of $Pb_{0.7}La_{0.3}Fe_{12}O_{19}$

Table 1: Activation energies of the electrical conductivity for $Pb_{0.7}La_{0.3}Fe_{12}O_{19}$ (PbLaM), $PbFe_{12}O_{19}$ (PbM) and $BaFe_{12}O_{19}$ (BaM)

E_A [eV]	$17 \div 50$ K	$50 \div 120$ K	$120 \div 289$ K
PbLaM, $x = 0.3$	0.008	0.029	0.129
PbM (ref. [1])	-	-	0.27
BaM (ref. [1])	-	-	0.67

like. In accordance with ref. [5] the conductivity σ can be described in both band model and electron hopping model by the formula $\sigma = AT^{-1}\exp[-E_A/k_BT]$, where A stands for structural constant, T for absolute temperature, k_B for Boltzmann's constant and E_A for activation energy. The parameter E_A characterizes the charge carriers; in the case of band model E_A describes the behaviour of their concentration, while in the case of electron hopping model that of their mobility. The measured data were fitted by a function of the type $\sum_i[a_iT^{-1}\exp(b_iT^{-1})]$. In order to achieve agreement of measured data with calculated curve as shown in Fig. 2, three terms in the sum were necessary. Fitted parameters a_i describe the conductivity mechanism from the point of view of crystal structure and carrier concentration, parameters b_i can be directly used for the calculation of the activation energies. The results are summarized in table 1.

The Mössbauer spectrum of powder sample taken at room temperature could be well described by five sextets according to the crystallographic sites of iron in hexagonal ferrite, together with a small paramagnetic component. The area of this component

does not exceed 1% of the total spectrum area. Instead of the usual Lorentzian lineshape, Voight line profile [6] was used, which yielded a better description of the broad 2a subspectrum [3]. The processing of the spectra measured at lower temperatures was complicated by the increasing overlap of the subspectra with the decrease of the temperature. For this reason the relative areas of subspectra 12k, $4f_2$, $4f_1$ and $2a$ were held in the ratio 6:2:2:1 during the spectra fitting. At lower temperatures ($5 \div 85$K) it was necessary to add another sextet to the spectra. The additional sextet was very broad and its relative area corresponded to the La concentration in the sample. The introduced area ratio 6:2:2:1 is not correct in this case because one of the areas present, most probably that of 2a site, is to be diminished by the area of the additional sextet ($6 : 2 : 2 :\approx 0.7$). Nevertheless, due to the strong overlap of the relevant subspectra this discrepancy makes no significant difference in spectra processing quality (χ^2). The temperature dependence of the hyperfine parameters of $Pb_{0.7}La_{0.3}Fe_{12}O_{19}$ is shown in Fig. 3.

In the temperature dependence of conductivity three temperature intervals with different activation energies were found. If we look more closely on the temperature dependence of the Mössbauer hyperfine parameters, we can also recognize three similar temperature intervals. At the lowest temperatures (5 and 20 K) we have a well resolved additional sextet with clear values of hyperfine parameters and intensity, which can be attributed to Fe^{2+} ions. In the middle temperature region (50 and 85 K) the parameters of additional sextet are dramatically changing and becoming nearer to those of subspectrum $2a$. The raised probability of electron hopping may be responsible for this effect. At high temperatures (160 K, 220 K, 290 K) the additional sextet completely disappears and five sextets are sufficient to describe the Mössbauer spectrum. In comparison with undoped ferrite the most significant changes are observed in the $2a$ sublattice where a remarkable increase in isomer shift and a decrease of hyperfine magnetic field are simultaneously accompanied by line broadening.

From these observations it can be concluded that in the temperature region of $5 \div 50$ K there is a stable position of Fe^{2+} ions (at least within the characteristic Mössbauer time), in the temperature interval of $50 \div 120$ K the enhancement of conductivity occurs as a consequence of the charge carriers release (some of 2a iron atoms undergo electron hopping) and in the temperature range of $120 \div 290$ K the conductivity raises mainly due to the enhanced charge carriers mobility (electron hopping frequency).

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