ELECTRIC CONDUCTIVITY AND THERMOELECTRIC POWER OF FERRIMAGNETICS WITH MAGNETOPLUMBITE STRUCTURE

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Electric conductivity and thermoelectric power are measured in single crystal specimens of $MeFe_{12}O_{19}$ (Me-Pb, Ba and Sr) ferrites from room temperature to 950°K, revealing an anisotropy of the two properties: $\sigma_{\perp c} > \sigma_{\parallel c}$ and $|\Theta_{\parallel c}| < |\Theta_{\perp c}|$ respectively. Assuming a conductivity of the "hopping" type, the change in electric current carrier generation energy due to decay of exchange interaction was determined and found to be anisotropic on transition through T_c, and much larger than the exchange energy corresponding to the transition temperature.

1. Introduction

Investigation of the electric properties of ferrites is of importance because, here, we are dealing with ferrimagnetics which present semiconductor properties. The 3*d* electrons of transition metal ions taking part in the exchange interactions which lead to magnetic ordering are at the same time electric current carriers. The topics of interest reside in the nature of the interaction between the carriers and the magnetic structure of the ferrimagnetic, and in the effect of crystallographical structure on this interaction.

The effect of magnetic ordering on current carriers has been studied for Ni–Zn ferrites [1], which have spinel structure.

The influence of crystallographical structure on the electric conductivity of ferrites was studied for hexagonal structure and exhibited anisotropy which, for *M* type structure, amounted to $\sigma_{\perp c} \approx 10\,\sigma_{\parallel c}$ [2] and for *W* type structure $\sigma_{\perp c} \approx 10^2 \div 10^3 \sigma_{\parallel c}$ [3]. Anisotropy of thermoelectric power was found by Zaveta [2] and Bunget [4] for *M* type structure.

This paper contains results on the temperature dependence of electric conductivity and thermoelectric power for single crystal specimens of $BaFe_{12}O_{19}$, $PbFe_{12}O_{19}$ and $SrFe_{12}O_{19}$, which have the hexagonal *M* type structure.

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From the temperature dependence of these two quantities and assuming conductivity of the "hopping" type, the energy Δ of carrier generation for direction parallel and perpendicular to the c-axis as well as its variation due to decay of magnetic ordering above T_c were calculated.

2. Experimental

1. Preparation of specimens

Specimens for measurement, about $0.5 \times 2 \times 4$ mm in size, were prepared from single crystals provided by the Institute for Semiconductors of the Academy of Sciences of the USSR, Leningrad. The single crystals had been obtained by crystallization from a solution of the molten oxides and presented optically smooth surfaces with no traces of macroscopic defects.

The electrodes were deposited by heating silver paste at 950°K.

2. Method of measuring Θ and σ

Measurements of electric conductivity σ and thermoelectric power Θ *versus* the temperature were performed successively at each of the fixed temperatures when heating and cooling, throughout a temperature range comprising T_c, for directions parallel and perpendicular to the c-axis. The variation of σ was calculated from changes in resistivity of specimens measured with a Wheatstone bridge. The thermoelectric power coefficient Θ was calculated from the thermoelectric power values measured with a photoelectric compensator. Temperature was measured by means of chromonickeline-constantan thermocouples and a compensator to within ± 2 deg. The difference in temperature of the ends of the specimen which amounted to about 10 deg was determined to within ± 0.05 deg.

3. Results of measurements

The results obtained in determining the temperature dependence of electric conductivity σ for various crystallographical directions are shown in Figs 1–3, and the results for ΘT *versus* T in Figs 4–6. The graphs reveal that the ferrimagnetics under investigation are semiconductors in which magnetic ordering exerts a marked influence on the thermoelectric properties but a weaker influence on electric conductivity. The two properties depend one the direction in the crystal; generally, one has:

$$|\Theta_{\parallel c}| < |\Theta_{\perp c}| \text{ and } \sigma_{\parallel c} < \sigma_{\perp c}$$

One will note a slight though well-defined dependence of the temperature of inflection of the ΘT *versus* T curve on the crystallographical direction. This inflection occurs at temperatures of several degrees higher for the direction perpendicular to the c-axis than for the direction parallel to it.

The activation energy of electric conductivity depends but weakly on the crystallographical direction.

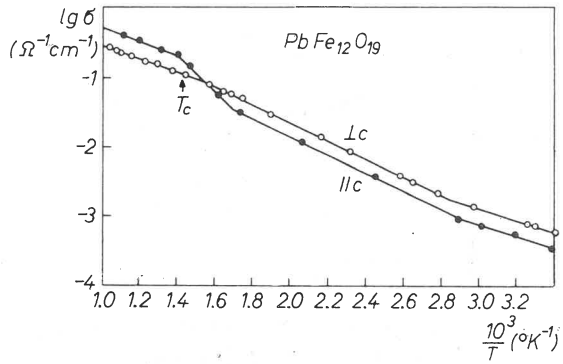

Fig. 1. Temperature-dependence of electric conductivity for $PbFe_{12}O_{19}$ ferrite single crystal for various crystallographical directions

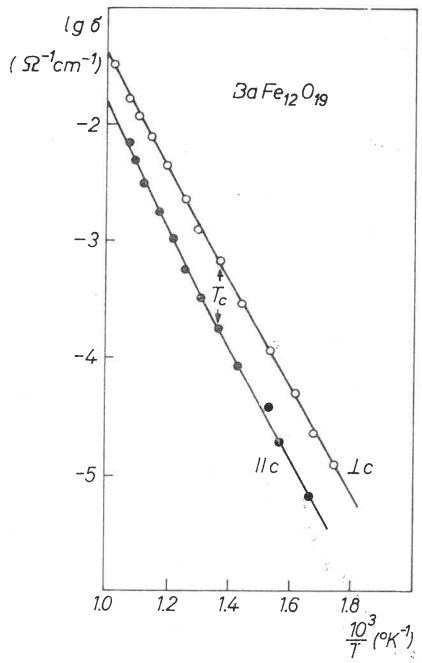

Fig. 2

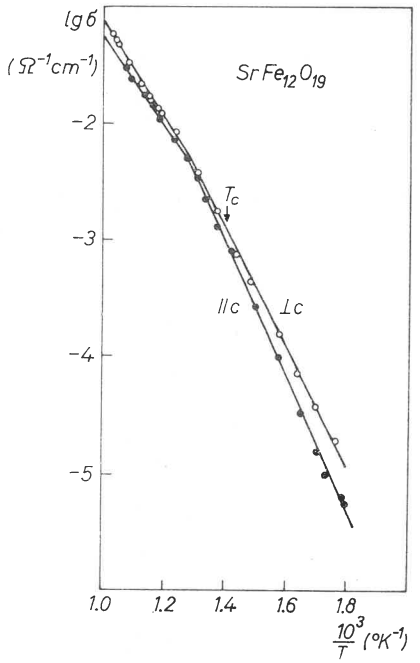

Fig. 3

Fig. 2. Temperature-dependence of electric conductivity for $BaFe_{12}O_{19}$ ferrite single crystal for various crystallographical directions

Fig. 3. Temperature-dependence of electric conductivity for $SrFe_{12}O_{19}$ ferrite single crystal for various crystallographical directions

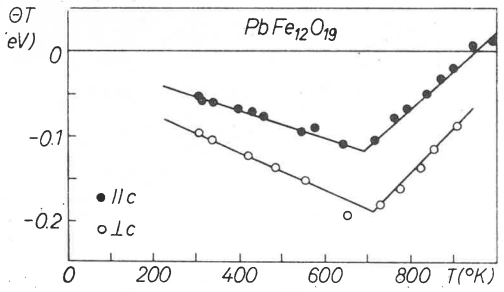

Fig. 4. Temperature-dependence of ΘT (Peltier coefficient) for $PbFe_{12}O_{19}$ ferrite single crystal for various crystallographical directions

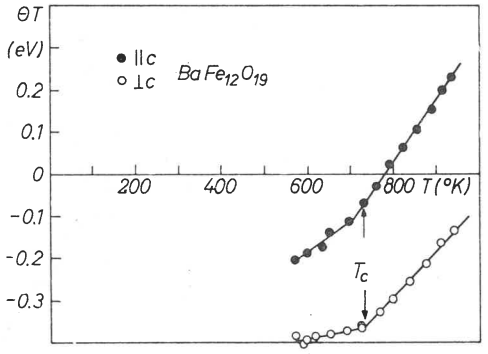

Fig. 5. Temperature-dependence of ΘT (Peltier coefficient) for $BaFe_{12}O_{19}$ ferrite single crystal for various crystallographical directions

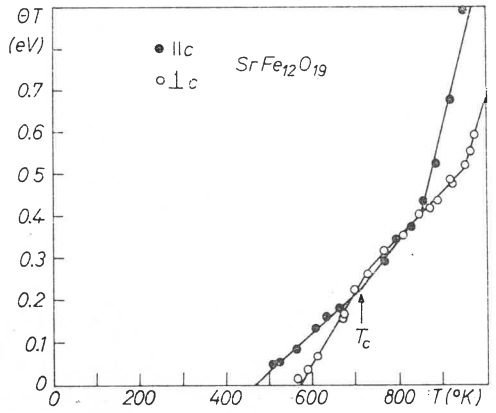

Fig. 6. Temperature-dependence of ΘT (Peltier coefficient) for $SrFe_{12}O_{19}$ ferrite single crystal for various crystallographical directions

4. Interpretation of the experimental results

Since the specimens have very low electric conductivity, we base our interpretation of the results on the assumption that conductivity in the ferrite specimens was of the "hopping" type. In such semiconductors, according to the theory of Tsuji [5],

$$\Theta T = \frac{\sigma_d(Q_d+\mu-E_1)-\sigma_e(Q_e+E_2-\mu)}{\sigma_d+\sigma_e}$$

with σ_d, σ_e the conductivity due to holes and electrons respectively, μ the chemical potential, E_1 the excited level energy of the Fe^{2+} ion and E_2 that of the Fe^{3+} ion.

Q_e and Q_d are given by

$$Q_e = -k\frac{d\ln W_e}{d(1/T)}, \quad Q_d = -k\frac{d\ln W_d}{d(1/T)}$$

where W_e and W_d are the probabilities of the jamping of an electron and a hole from an ion site to adjacent one per unit time.

The energy of current carrier generation Δ was determined from the curves of ΘT *versus* T for various ranges of temperature as $\Delta_e = E_2-\mu$ when the carriers were electrons and $\Delta_d = \mu-E_1$ when they were holes.

The electric conductivity of semiconductors of the type under consideration is described by a formula due to Heikes and Ure [6]:

$$\sigma = \sigma_\infty \exp\left(-\frac{q}{kT}\right)$$

where

$$\sigma_\infty = \text{const}\, n(N-n)T^{-1}\tau_0^{-1}$$

and q is the activation energy of the electric conductivity process involving the carrier generation energy Δ and the activation energy describing the change in mobility of the carriers with temperature n is the concentration of carriers, $N-n$ the number of sites into which a carrier can hop, τ_0^{-1} an *a priori* probability for the occurrence of a hopping act at infinite temperature *i.e.* the upper limit of the hopping frequency value.

Below, we give the values of variations in carrier generation energy *versus* the crystallographical direction at transition through T_c:

	variation $\lvert\Delta_{\parallel c}\rvert$ eV	variation $\lvert\Delta_{\perp c}\rvert$ eV
$PbFe_{12}O_{19}$	0.372	0.565
$BaFe_{12}O_{19}$	0.440	0.743
$SrFe_{12}O_{19}$	0.260	0.420

It is noteworthy that these variations in carrier generation energy considerably exceed the exchange energy corresponding to T_c.

The explanation of the anisotropic thermoelectric and electroconductive properties will be based on the assumption that the "hopping" model is applicable to these properties in ferrimagnetics with hexagonal M type structure.

A reason for these anisotropies can be sought for primarily in the crystallographical structure, which defines the exchange interactions between Fe ions. Zaveta [2], from considerations of hexagonal lattice geometry, derives the conclusion that these interactions are weaker in the plane parallel to the c-axis than in the plane perpendicular to it, owing to larger distance. His conclusion is corroborated by the results of Belov *et al.* [7], who studied the dependence of Curie temperature on the crystallographical direction for these structures and found that T_c for the direction parallel to the c-axis was by several degrees lower than T_c for the direction perpendicular there to. This experimental fact corroborates Zaveta's conclusion [2].

The above anisotropy of exchange interactions between Fe ions explains the small difference in temperatures in which the anomaly of thermoelectric properties occurs (Figs 4–6). This anomaly occurs at a lower temperature for the direction parallel to the c-axis than perpendicular to it. Such an anomaly points to an influence of exchange interaction between nearest neighbours on the electric current carriers hopping between neighbouring Fe^{2+} and Fe^{3+} ions.

With regard to the anisotropy in electric conductivity of the ferrimagnetics, the results of others as well as those of this study lead to the assumption that it is due to the value of the factor σ_∞ in the formula of the conductivity *versus* temperature. This assumption is supported by the fact that the activation energy q is independent of or very weakly dependent on the crystallographical direction and that it is hardly possible to assume the existence of anisotropy of the carrier density n. One still has to consider the term in τ_0^{-1}, which defines the hopping probability. The anisotropy of τ_0^{-1} (τ_0^{-1} for the direction parallel to the c-axis smaller than for the perpendicular one) implies that the hopping probability of the carriers is itself anisotropic. Thus, a carrier hops more often in the plane perpendicular to the c-axis, yielding macroscopically a larger value of the electric conductivity in this direction. This is clear once one assumes that, in this plane, the separation of Fe^{2+} ions and Fe^{3+} ions is less, permitting a larger overlapping of their orbitals. This result is in accordance with the results of Belov *et al.* [7].

The assumption of the anisotropy of τ_0^{-1} moreover explains in a simple manner the anisotropy of the thermoelectric power coefficient Θ, $|\Theta_{\perp c}| > |\Theta_{\parallel c}|$; indeed, in Tsuji's expression [5], Q_e and Q_d depend hopping probabilities of the carriers, like τ_0^{-1} in the expression for σ_∞.

5. *Conclusions*

The preceding qualitative considerations show that, by assuming the "hopping" model for ferrimagnetic semiconductors with hexagonal structure, their anisotropic properties such as anisotropic electric conductivity, anisotropic thermoelectric power, and anisotropic exchange interactions between iron ions apparent as anisotropic Curie temperature, can be simply explained.

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