New mechanism of low-temperature transformation in ferrites containing Mn^{3+} ions

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We investigated the behavior of the temperature dependences of the electric resistivities of four samples: $Cu_{0.8}Fe_{1.6}O_4$, $Cu_{0.67}Fe_{1.34}Mn_{0.99}O_4$, $Cu_{0.4}Fe_{0.4}Cr_{0.4}Mn_{1.8}O_4$, and $Cu_{3/8}Fe_{3/8}Cr_{3/8}Mn_{15/8}O_4$. We observed abrupt changes in the resistivity of all samples in the region 100–150°K. On the basis of our results and those of Buchenau et al., it is proposed that the anomalous behavior of the resistivity is due to the onset of negative Mn^{3+}–Mn^{3+} cation-cation interaction in the B sites.

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Much attention is being paid presently to the possibility, at low temperatures, of direct exchange between magnetic cations in ionic oxide compounds, an exchange that can exert a strong influence both on the character of the magnetic ordering and on the electric resistivity.[1-3] For example, in recent papers[2,3] a new explanation was proposed for the low-temperature transformation in magnetite, using an idea by Goodenough,[4] according to which low-temperature conversion can occur in ionic compounds as a result of formation of homopolar bond due to direct overlap of the t_{2g} orbitals of $3d$-cations located in octahedral sites of crystal lattice.

One of the significant attributes of this transformation is the abrupt change of the resistivity and of the type of conductivity as a result of the joining of the greater part of the d-electrons of the low-temperature phase in homopolar bonds.

As is well known, in ferrites with spinel structure, direct exchange can exist between $3d$ cations located in B-sites. On this basis, we propose that a low-temperature transformation due to the appearance of homopolar cation-cation bonds will always be observed in ferrites.

To check on the validity of our assumption, we investigated samples of the following systems:

1. $(1-x)CuFe_2O_4 + xMn_3O_4$ $(x = 0.20;\ 0.33)$,
2. $(1-x)CuFeCrO_4 + xMn_3O_4$ $(x = 0.60;\ 5/8)$.

According to the results of[5,6], the ions $Mn^{2+}(d^5)$ and $Mn^{3+}(d^4)$ exist simultaneously in the B-sites of these ferrites.

Our samples were prepared by a ceramic technology, with the centering procedure taken from[5,6]. The electric contacts were deposited with the aid of a paste consisting of 80% In and 20% Ga.

It is seen from Fig. 1, which shows the temperature dependences of $\ln\rho(1/T)$ of the samples of the system 1, that in the low temperature region, just as in magnetite, there is observed an abrupt change of the resistivity ρ and an appreciable change in the activation energy E. Such an anomalous behavior of the value of ρ of the investigated ferrites is apparently due to the destruction of the cation-cation Mn^{3+}–Mn^{3+} ion interaction, as a result of which the number of d electrons that take part in the conductivity increases.

According to the Goodenough rules,[4] the 90° cation-cation Mn^{3+}–Mn^{3+} ion interaction should be negative, since these ions have an electron configuration $l_g^1 t_{2g}^3$, i.e., they have a half-filled t_{2g} orbital. We have thus found that at low temperature there exists in the B-sites a negative exchange interaction between the Mn^{3+} ions, which lead at $T < T_{tr}$ to a noncollinear magnetic ordering.

To verify this fact, we measured the magnetization curves $\sigma(H)$ and the magnetostriction curves $\lambda_{\parallel}(H)$ and $\lambda_{\perp}(H)$. It turned out that in fields stronger than the technical-magnetization fields there is no saturation on the $\sigma(H)$ curves, and the magnetostriction has no isotropic character. This behavior of $\sigma(H)$, $\lambda_{\parallel}(H)$, and $\lambda_{\perp}(H)$ offers evidence of the presence of low temperatures of the power process. As to the region $T > T_{tr}$, only saturation is observed in that region on the $\sigma(H)$, $\lambda_{\parallel}(H)$, and $\lambda_{\perp}(H)$ curves.

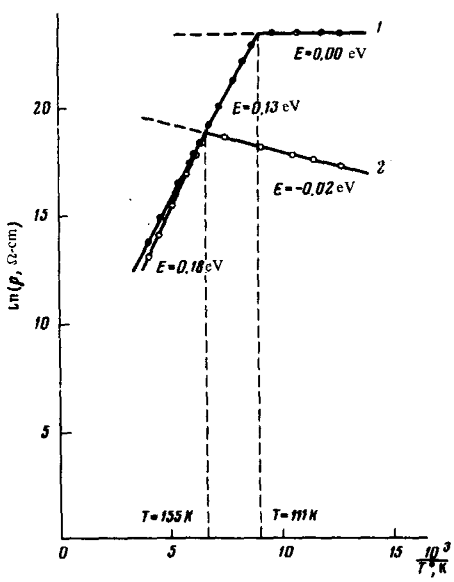

FIG. 1. Temperature dependence of lnρ for the following samples: 1) $Cu_{0.8}Fe_{1.6}Mn_{0.6}O_4$; 2) $Cu_{0.67}Fe_{1.34}Mn_{0.99}O_4$.

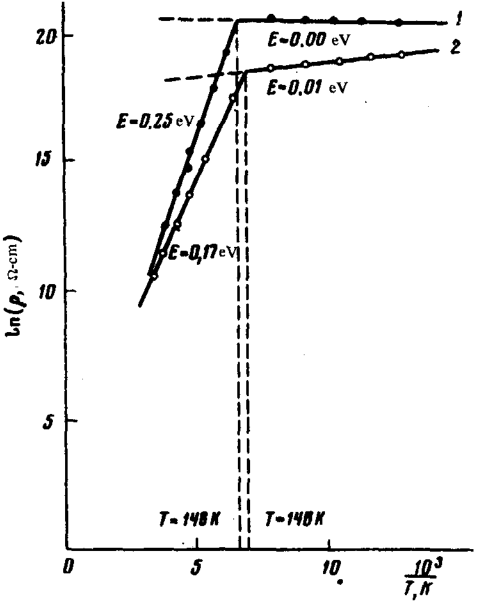

FIG. 2. Temperature dependence of lnρ for the following samples: 1) $Cu_{3/8}Fe_{3/8}Cr_{3/8}Mn_{15/8}O_4$; 2) $Cu_{0.4}Fe_{0.4}Cr_{0.4}Mn_{1.8}O_4$.

Thus, in the investigated ferrites, as a result of formation of homopolar cation-cation bonds in the *B*-sites, an abrupt change takes place in the resistivity and in the magnetic structure, which becomes noncollinear.

A similar behavior of the resistivity was obtained also for samples of system 2 (Fig. 2).

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