# On the nature of the anomalous negative magnetoresistance and para-process in magnetite and manganese ferrite at low temperatures

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Based on analysis of experimental measurements of the electrical and magnetic properties of magnetite and manganese ferrite, the conclusion is reached that a new mechanism of the para-process and negative magnetoresistance exists in these magnets at low temperatures. This mechanism is based on the delocalization by the external magnetic field of $t_{2g}$ electrons paired in cation-$B$–cation-$B$ covalent bonds.

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The large negative magnetoresistance and the significant para-process on the magnetization ($\sigma$) isotherms that have been observed at low temperatures in magnetite[1–3] and manganese ferrite[4,5] are among the most hard-to-explain anomalies in spinel ferrites. Despite the large number of studies of these effects, their nature still remains unclear.

In the present study we measured the magnetization $\sigma$, the magnetoresistance $\Delta R/R$, and the magnetostriction $\lambda$ for the same samples of magnetite and manganese ferrite. The samples were prepared by ceramic techniques. The first and second annealing of the $Fe_3O_4$ sample were done in a medium of $CO_2 + H_2$ at temperatures of 1100 and 1300 °C, respectively. The $MnFe_2O_4$ sample was first annealed in air at 1000 °C and finally sintered in a vacuum at 1350 °C.

Figure 1 shows the 80 K isotherms of $\sigma(H)$ and of the longitudinal and transverse magnetoresistance $(\Delta R/R)_{\parallel}$, $(\Delta R/R)_{\perp}$ and magnetostriction $\lambda_{\parallel}$, $\lambda_{\perp}$ of the manganese ferrite samples. The analogous results for magnetite (Fig. 2) are given for a temperature of 130 K, where the sample has an undistorted cubic structure. It is seen that both samples have anomalously large magnetoresistances, with $(\Delta R/R)_{\parallel}$ and $(\Delta R/R)_{\perp}$

  

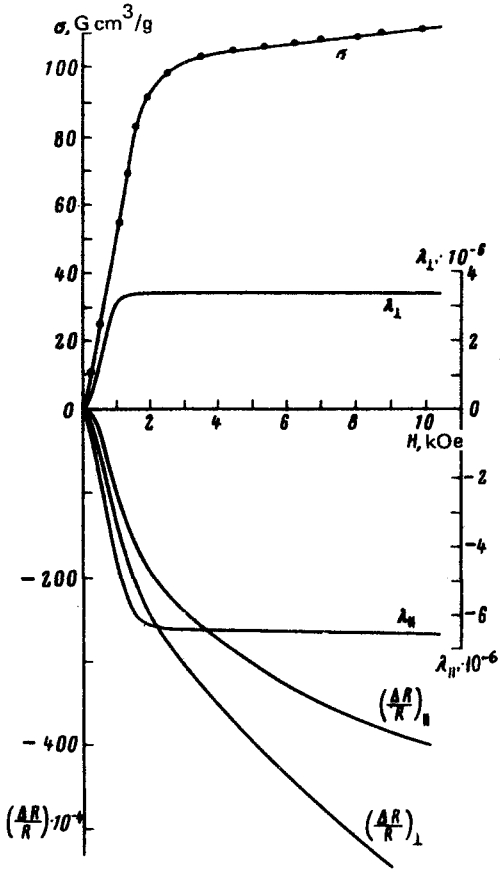


FIG. 1. Isotherms of the magnetization $\sigma$ and of the longitudinal and transverse magnetoresistance $(\Delta R/R)_{\parallel}$, $(\Delta R/R)_{\perp}$ and magnetostriction $\lambda_{\parallel}$, $\lambda_{\perp}$ of the manganese-ferrite sample, taken at 80 K.

being approximately equal in size and displaying a nonlinear behavior in strong fields. One notices that whereas a para-process occurs on the $\sigma(H)$ isotherms, the magnetostriction in strong fields remains constant. The fact that the para-process does not display magnetostriction is evidence of collinear spin ordering in magnetite and magnesium ferrite at the given temperatures, in agreement with the results of neutron-diffraction[6] and Mössbauer[7] studies. Consequently, the para-process and the negative magnetoresistance in these compounds are not due to the presence of noncollinear spin ordering.

As was first shown by Goodenough,[8] oxide compounds with the spinel structure can undergo phase transitions due to the formation of stable cation-$B$–cation-$B$ covalent bonds in the octahedral ($B$) sublattice at a certain temperature $T_{tr}$. The appearance of these bonds is due to the direct overlap of the $t_{2g}$ orbitals of the $3d$ cations found at neighboring $B$ sites. As a result, the $t_{2g}$ electrons become localized in these bonds; such a localization in turn leads to a sharp rise in the electrical resistivity of ferrites. If the overlapping $t_{2g}$ orbitals have one electron apiece (as, for example, in the

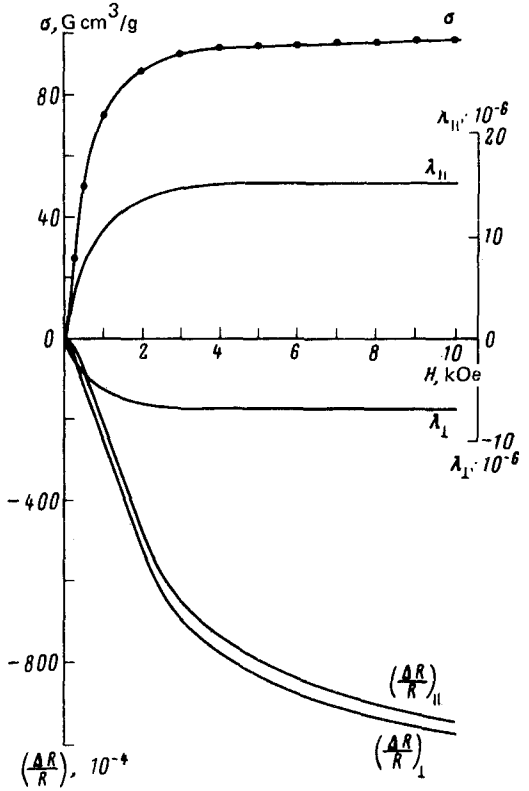


FIG. 2. Isotherms of the magnetization $\sigma$ and of the longitudinal and transverse magnetoresistance $(\Delta R/R)_{\parallel}$, $(\Delta R/R)_{\perp}$ and magnetostriction $\lambda_{\parallel}$, $\lambda_{\perp}$ of the magnetite sample, taken at 130 K.

cations $Fe^{3+}$ and $Mn^{2+}$ with electron configuration $e_g^{\,2+}t_{2g}^{\,3+}$), the spins of these electrons become paired, leading to a decrease in the magnetic moments of the interacting cations. We have established in an earlier paper[9] that the formation of the covalent bonds $Fe_B^{\,2+}$–$Fe_B^{\,2+}$ and $Fe_B^{\,3+}$–$Fe_B^{\,3+}$ in magnetite occurs at temperatures of $\simeq$170 and $\simeq$140 K, respectively. In manganese ferrite the covalent bonds $Mn_B^{\,2+}$–$Mn_B^{\,2+}$ and $Fe_B^{\,3+}$–$Fe_B^{\,3+}$ are formed at $\simeq$240 and $\simeq$145 K, respectively.

It is known that a magnetic field causes a compression of the electronic wave functions.[1)] One would therefore expect that the application of an external magnetic field in spinel ferrites at $T<T_{tr}$ should decrease the overlap of the $t_{2g}$ orbitals in the cation-cation pairs. This in turn should lead to a partial delocalization of the electrons and, hence, to a decrease in the electrical resistivity, i.e., to a negative magnetoresistance. This assertion is in agreement with the conclusions of theoretical studies[11,12] of the negative magnetoresistance of semiconductors, which have shown that in cases where the negative magnetoresistance is primarily due to delocalization of electrons by the magnetic field, the longitudinal and transverse magnetoresistances should be similar in magnitude. The theory also implies that the magnetoresistance isotherms in strong fields should be nonlinear, as is seen in magnetite and manganese ferrite at $T<T_{tr}$.

In summary, we have proposed in this paper a new mechanism for the paraprocess and negative magnetoresistance in spinel ferrites at $T < T_{tr}$, based on the delocalization by the external magnetic field of $t_{2g}$ electrons paired in cation-*B*–cation-*B* covalent bonds.

[1)]This question was examined theoretically in Ref. 10.


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