On the nature of low-temperature transitions in $CuFe_2O_4$ ferrite

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A comprehensive study of a tetragonally distorted ferrite $CuFe_2O_4$ for $T \ll T_C$ ($T_C = 710$ K) has led us to a conclusion that three low-temperature second-order transitions occur in this material: a) the first transition takes place at $T_{t1} = 350 \pm 5$ K and is due to the spin-orbit coupling of Cu^{2+} octahedral ions; b) the second transition takes place at $T_{t2} = 240 \pm 5$ K and is caused by an increase in the degree of covalence between the Cu_B^{2+} and O^{2-} ions; 3) the third transition occurs at $T_{t3} = 170 \pm 5$ K and is caused by formation of a noncollinear magnetic structure. © *1996 American Institute of Physics.* [S1063-7761(96)01112-2]

Although the $CuFe_2O_4$ copper ferrite has been studied for a considerable time, little is known about its magnetic properties at temperatures much lower than the Curie temperature $T_C = 710$ K, particularly below room temperature.

Earlier[1] we detected a spin-reorientation transition at a temperature around 350 K. We determined that in this temperature range the magnetization vector turned from the [111]- axis to the [001]-axis.

Measurements of the magnetocaloric effect (ΔT-effect) in a $CuFe_2O_4$ polycrystalline sample with a tetragonally distorted spinel structure demonstrated that at a temperature $T \approx 330$ K, when the magnetization vector deviated from the [111]-direction, the sign of the magnetocaloric effect changed from plus to minus.

Previously[2] we found out that, concurrently with the spin-reorientation transition, the magnetoresistance grew sharply at temperature around 340 K and the activation energy also changed.

In studying the magnetostriction as a function of temperature we determined[3] that as the temperature of a tetragonally distorted copper ferrite sample decreased, the magnetostrictions $\lambda_\perp$ and $|\lambda_\parallel|$ first increased rapidly, then below $T = 250$ K they dropped considerably.

The cause of this anomalous behavior of both magnetostriction and magnetic anisotropy of the copper ferrite at temperatures considerably lower than the Curie temperature remained unclear. It seemed interesting, therefore, to measure concurrently the magnetic parameters and linear thermal expansion of the same copper-ferrite sample.

The conditions for synthesis of tetragonally distorted copper ferrite and techniques for measuring its magnetic properties are given elsewhere.[3] The relative uncertainties in measurements of magnetization and magnetostriction were about 3%, and the errors in measurements of magnetoresistance and magnetocaloric effect were about 4%.

Figure 1 shows the spontaneous magnetization σ_s, coercive force H_c, and magnetostrictions $\lambda_\perp$ and $\lambda_\parallel$ ($H = 10$ kOe) versus temperature. It can be seen that H_c, $\lambda_\perp$, and $|\lambda_\parallel|$ grow rapidly at temperatures around 350 K. But unlike our previous results,[3] $\lambda_\perp$ drops at temperatures below 293 K, and $|\lambda_\parallel|$ decreases below 225 K. As concerns the coercive force, it grows monotonically as the temperature drops.

The copper ferrite $Fe^{3+}[Cu^{2+}Fe^{3+}]O_4^{2-}$ contains tetrahedral Fe_A^{3+} and octahedral Fe_B^{3+} ions whose ground state is an orbital singlet, and octahedral Cu_B^{2+} ions whose orbital doublet splits into two singlets at temperatures below that of the Jahn–Teller transition in the copper ferrite ($T \approx 650$ K). Therefore in the first approximation the orbital moments of Fe_A^{3+} Fe_B^{3+}, and Cu_B^{2+} ions should be frozen by the crystal field, so the spin–orbit coupling should be practically zero. ESR data, however, indicate[4] that the spin-orbit coupling admixes some of the triplet states to the doublet ground state of Cu_B^{2+}. As a result, not only is its g-factor different from 2, but it is also anisotropic. Thus the ESR data indicate that the Cu_B^{2+} orbital moment is not frozen completely, i.e., there is nonzero spin–orbit coupling.

Our measurements and ESR data indicate that the spin reorientation transition in the copper ferrite at $T_{t1} = 350 \pm 5$ K is due to the spin–orbit coupling of Cu_B^{2+} ions.

The decrease in $\lambda_\perp$ and $|\lambda_\parallel|$ at lower temperatures demonstrates, however, that the relative contribution of the spin–orbit coupling of Cu_B^{2+} ions drops.

Since the sharp drop in $\lambda_\perp$ and $|\lambda_\parallel|$ with temperature occurs at different temperatures, the transition temperature T_{t2} is determined more accurately using the anisotropic (total) magnetostriction $\lambda_t = \lambda_\parallel - \lambda_\perp$ as a function of temperature. Figure 2 shows the curve of $\lambda_t(T)$ calculated at $H = 10$ kOe. It is seen that $|\lambda_t|$ drops below 240 K. One may assume, therefore, that in the copper ferrite a second low-temperature transition occurs at $T_{t2} = 240 \pm 5$ K. In this graph the curve of the volume magnetostriction $\omega = \lambda_\parallel + 2\lambda_\perp$ versus temperature is also given. Its shape is quite different from that of $\lambda_t(T)$. The volume magnetostriction ω proved to be negative throughout the studied temperature range and its absolute value rapidly increases with a decreasing temperature below 150 K.

It is known that ferrites with the spinel structure are ionic compounds with a notable admixture of covalence in the cation–anion bond. In ionic compounds the formation of a covalent bond implies that the electron is no longer localized at the central $3d$-ion and does not change its spin magnetic moment, whereas its orbital moment drops.[5]. Hence the degree of covalence should affect the spin–orbit coupling amplitude. From our data on magnetostriction, we assumed that the degree of covalence in the bond between Cu^{2+} and O^{2-} in the copper ferrite increases for $T \leqslant T_{t2}$, which, in

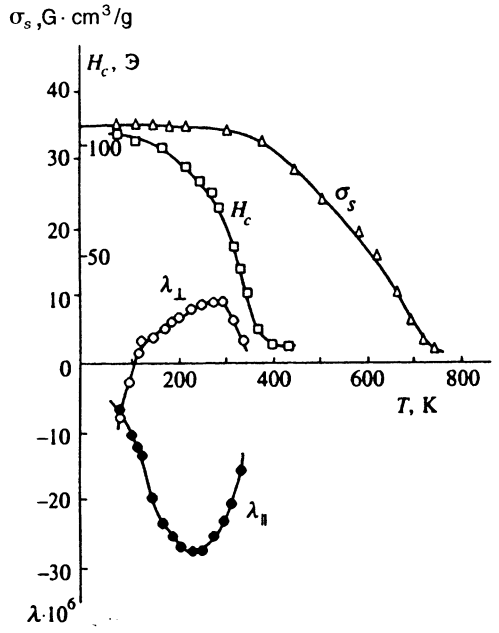

FIG. 1. Spontaneous magnetization σ_s, coercive force H_c, perpendicular $\lambda_\perp$ and parallel $\lambda_\parallel$ magnetostrictions as functions of temperature measured under a magnetic field $H = 10$ kOe.

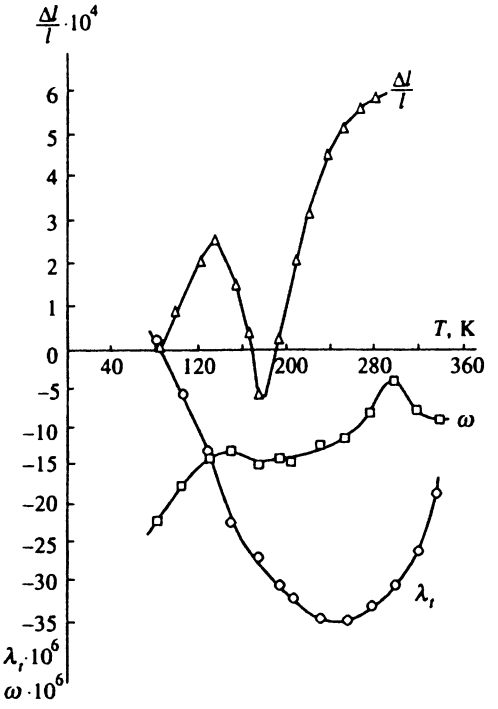

FIG. 2. Anisotropic λ_t and volume ω magnetostrictions versus temperature measured at $H = 10$ kOe and relative thermal expansion $\Delta l/l$.

turn, leads to a decrease in the spin–orbit coupling of Cu $^{2+}_{B}$ ions. This assumption is in agreement with the data of Sahastabunde and Vaingahar,[6] who found from the X-ray diffraction patterns that, in comparison with other simple ferrites, the copper ferrite has a considerably higher degree of covalence in the bond. They supposed that it was caused by the smaller difference between electronegative parameters of copper (−1.75) and oxygen (−3.5) than in the case of Co (−1.7), Zn (−1.66), and Mn (−1.6).

This change in the degree of covalence should, probably affect the crystal lattice of the ferrite. This assumption was tested by measuring the linear thermal expansion $\Delta l/l$ in a temperature range of 80–293 K (Fig. 2). One can see that the sample contracts rapidly with decreasing temperature between 240 and 170 K. It is interesting that in the temperature range where the values of magnetostrictions $|\lambda_\parallel|$, $\lambda_\perp$, and $|\lambda_t|$ drop with decreasing temperature, the thermal expansion coefficient $\alpha = d[\Delta l/l(T)]/dT$ is highest ($\alpha \approx 10 \times 10^{-6}$). From this we conclude that the increase in the degree of covalence of the cation–anion bond in the copper ferrite leads to a larger compression of the crystal lattice.

Our measurements of the thermal expansion lead to the conclusion that a third low-temperature phase transition occurs in the copper ferrite at $T_{t3} = 170 \pm 5$ K. At the transition point the thermal expansion coefficient changes its sign from plus to minus.

Earlier[7] we determined that the $CuFe_2O_4$ magnetic structure at 80 K is noncollinear. Given that the bulk magnetostriction ω is negative, and the noncollinear magnetic structure occurs in the B-sublattice, we can assume that external magnetic field should reduce the noncollinearity of the magnetic structure, which is accompanied by the sample contraction. From this we conclude that the noncollinear magnetic structure produced in the copper ferrite during cooling should result in expansion of its crystal lattice. This suggestion is confirmed by measurements of thermal expansion (Fig. 2). One can see that the copper ferrite expansion coefficient α changes its sign from plus to minus at a temperature around 170 K, and at $T \leqslant 140$ K it is again positive. Thus we have found out that the sample expands as the temperature drops from 170 to 140 K. From this we conclude that the transition from the collinear to noncollinear magnetic structure (an order–order transition) occurs at T_{t3}.

It is known that the transition from the triangular structure to antiparallel one and vice versa at a certain temperature is in a sense similar to the ferromagnet–paramagnet

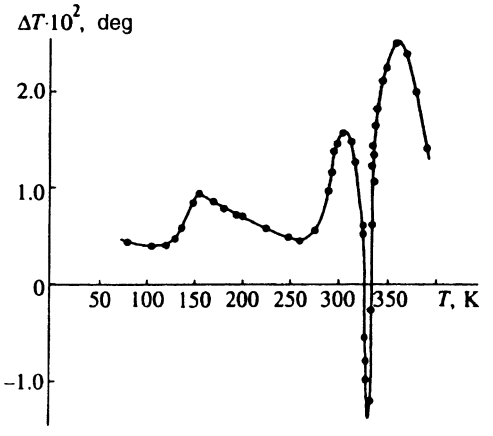

FIG. 3. Amplitude of the magnetocaloric (ΔT) effect versus temperature recorded at $H = 11$ kOe.

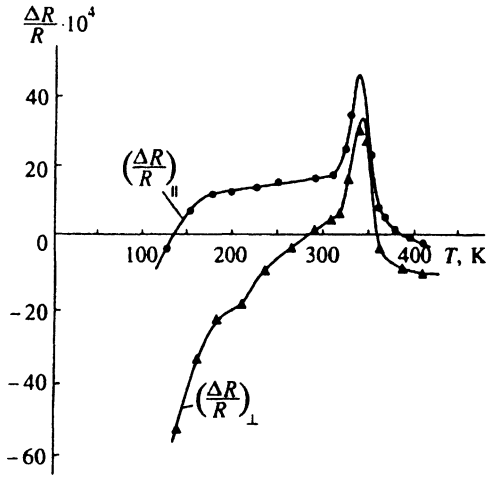

FIG. 4. Transverse $(\Delta R/R)_{\parallel}$ and longitudinal $(\Delta R/R)_{\perp}$ relative magnetoresistances as functions of temperature measured at $H=10$ kOe.

transition at the Curie point. This is a second-order transition.[8]

In their turn, second-order phase transitions demonstrate jumps in both the thermal expansion coefficient and heat capacity.[9] Therefore we have measured the magnetocaloric and galvanomagnetic effects at temperatures below the room temperature.

Figure 3 shows a curve of the ΔT-effect as a function of temperature recorded in a field $H=11$ kOe, which is considerably higher than the magnetic anisotropy field. There is a maximum on the curve of $\Delta T(T)$ at 150 K, which is a confirmation of our assumption about a second-order phase transition at this temperature related to the transition from the collinear to noncollinear magnetic structure as the temperature decreases.

This conclusion is in agreement with magnetoresistance data. Figure 4 shows the longitudinal $(\Delta R/R)_{\parallel}$ and transverse $(\Delta R/R)_{\perp}$ magnetoresistances recorded at $H=10$ kOe. It is evident that below a temperature of about 170 K both the transverse and longitudinal magnetoresistances rapidly change with decreasing temperature.

In order to determine the phase transition temperatures more accurately, we have measured the activation energy at temperatures ranging between 80 and 400 K. Figure 5 shows the curve of $\ln\rho(1/T)$. At temperatures $T_{t1}=350$ K, $T_{t2}=238$ K, and $T_{t3}=174$ K the changes in the activation energy are comparable to that at the Curie point.

To sum up, our comprehensive study of magnetic and electric parameters of the $CuFe_2O_4$ copper ferrite allows us to conclude that three low-temperature, second-order transitions occur in this material at $T \ll T_C$:

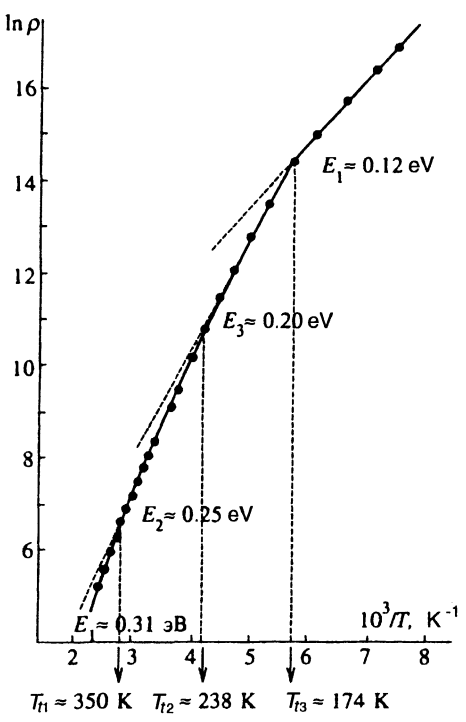

FIG. 5. Logarithm of sample resistivity as a function of $1/T$.

a) the first transition occurs at $T_{t1}=350\pm5$ K and is caused by spin–orbit interaction of Cu^{2+} octahedral ions;

b) the second transition takes place at $T_{t2}=240\pm5$ K, owing to an increase in the degree of covalence of the Cu_B^{2+}–O^{2-} bond;

c) the third transition occurs at $T_{t3}=170\pm5$ K and is due to formation of a noncollinear magnetic structure.

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