TEMPERATURE DEPENDENCE OF THE PARAMAGNETIC SUSCEPTIBILITY OF NICKEL-ZINC FERRITES

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Submitted to JETP editor May 5, 1958

J. Exptl. Theoret. Phys. (U.S.S.R.) **35**, 875-879 (October, 1958)

We have investigated the temperature dependence of the paramagnetic susceptibility of nickel-zinc ferrites. The results of the measurements are in good agreement with theory.

1. Numerous investigations of ferromagnetic metals and alloys at high temperatures $T \gg \Theta_f$ (where Θ_f is the ferromagnetic Curie point) have shown that their paramagnetic susceptibility obeys the Curie-Weiss law. The definite dependence on alloy composition which was established for the Curie-Weiss constant C and thus for the magnetic moment played an important part in the development of paramagnetic theory.

The temperature dependence of the paramagnetic susceptibility of ferrites cannot be described even approximatly by the Curie-Weiss law. The law that is obeyed by the paramagnetic susceptibility of ferrites was first established theoretically by Néel.[1] In Néel's theory the reciprocal of the susceptibility $1/\chi$ is a hyperbolic function of the temperature T:

$$1/\chi = 1/\chi_0 + T/C_N - \sigma/(T - \Theta), \tag{1}$$

where the constants σ, Θ, $1/\chi_1$ represent the following:

$$\Theta = nC_N\lambda\mu\,(2 + \alpha + \beta), \tag{2}$$

$$\sigma = n^2C_N\lambda\mu\,[\lambda(1+\alpha) - \mu(1+\beta)]^2, \tag{3}$$

$$1/\chi_0 = n\,(2\lambda\mu - \lambda^2\alpha - \mu\beta). \tag{4}$$

Here C_N is the atomic constant for magnetic Fe^{3+} ions; λ and μ are the numbers of these ions in sublattices A and B, respectively; n, α, and β are constants of the molecular field associated with the sum of the exchange integrals corresponding to interactions of the types AB, AA and BB, respectively. It has been shown[2,3] that Néel's equation (1) is a sufficiently good description of the experimentally observed paramagnetic properties of simple ferrites.

The dependence of the parameters C and Θ in the Curie-Weiss law on composition has played an important part in the development of paramagnetic theory, especially regarding the paramagnetism of alloys. At the present time we have no information regarding the dependence of the parameters in Néel's equation on the composition of mixed ferrites (ferrite alloys). Moreover, it would be of great interest to determine whether ferrites possess a transition region at temperatures very close to the Curie point where the magnetic susceptibility would depend on the magnetic field strength as in the case of ferromagnetic metals.[4] The present work was undertaken to answer the questions that have been indicated.

2. The temperature dependence of the paramagnetic susceptibility of ferrites was investigated with the apparatus described in reference 4. We investigated the mixed nickel-zinc ferrites $Fe_2O_3 \cdot (1-z)NiO \cdot zZnO$, where z varied from 0 to 1. The ferrites were compressed under a pressure of 3 tons/cm^2 and were baked at 1300°C for 3 hours, after which they were cooled slowly inside the furnace. The uniformity of the ferrites was then checked. Several samples were prepared from a ferrite of a given composition; these were investigated over a broad temperature range and the values of the susceptibility were compared. Repeated heating and cooling of the samples during the investigation did not affect the results; this was evidence of the absence of any phase transformation in the given temperature range.

Figure 1 shows the temperature dependence of the reciprocal of the molar susceptibility for all of the ferrites that we investigated from 300 to ≈ 1500°K. The curves of $1/\chi$ as a function of T are concave to the temperature axis. The curvature decreases gradually as more zinc oxide is added to the nickel ferrite and we have an almost linear dependence for a pure zinc ferrite. As already stated, in Néel's theory of ferrites the temperature dependence of the paramagnetic susceptibility obeys Eq. (1). Unfortunately the numerical values of the constants in the equation are not given by Néel's theory and must be determined

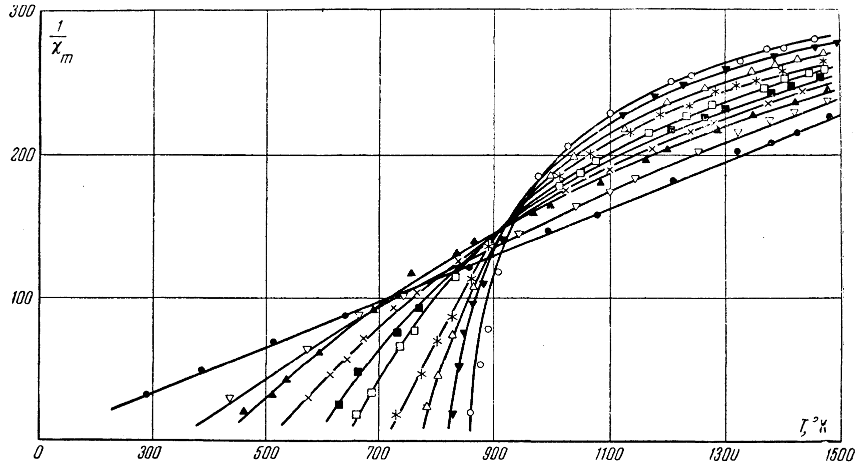

FIG. 1. Temperature dependence of the reciprocal susceptibility for the following ferrites: ○ – $Fe_2O_3 \cdot NiO$; ▼ – $Fe_2O_3 \cdot 0.9 NiO \cdot 0.1 ZnO$; Δ – $Fe_2O_3 \cdot 0.8 NiO \cdot 0.2 ZnO$; * – $Fe_2O_3 \cdot 0.7 NiO \cdot 0.3 ZnO$; □ – $Fe_2O_3 \cdot 0.6 NiO \cdot 0.4 ZnO$; ■ – $Fe_2O_3 \cdot 0.5 NiO \cdot 0.5 ZnO$; × – $Fe_2O_3 \cdot 0.4 NiO \cdot 0.6 ZnO$; ▲ – $Fe_2O_3 \cdot 0.3 NiO \cdot 0.7 ZnO$; ∇ – $Fe_2O_3 \cdot 0.2 NiO \cdot 0.8 ZnO$; ● – $Fe_2O_3 \cdot ZnO$.

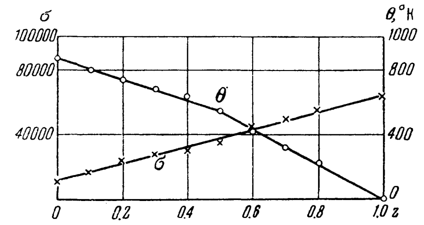

FIG. 2. Dependence of the constants σ and Θ on the percentage of zinc oxide.

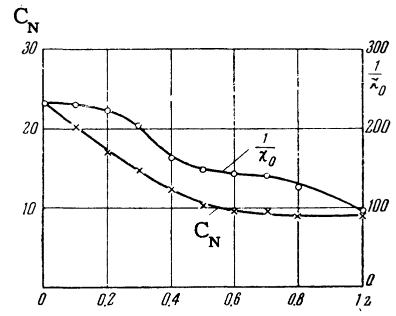

FIG. 3. Dependence of the constants C_N and $1/\chi_0$ on the percentage of zinc oxide.

experimentally. We obtained these constants by the method of successive approximations which was suggested by Néel[1] and which was described by us in detail in reference 3. It must be noted that when the constants obtained in this way are substituted into Néel's equation and the corresponding curves are plotted, the latter may not agree with the experimental curves from which the constants were determined by the graphical method referred to above. The degree of divergence of the curves can characterize the correctness of Néel's equation in each individual case.

Figures 2 and 3 show the dependence of the constants Θ, C_N, and $1/\chi_0$ on the percentage of ZnO in the ferrite. We note that while Θ and C_N decrease as the zinc oxide content increases, σ, on the other hand, increases. C_N must evidently indicate to some extent the magnitude of the paramagnetic moment. Figure 3 shows that as the amount of zinc oxide increases, C_N decreases. The reduction of C_N and thus of the paramagnetic moment evidently results from the fact that the addition of zinc, which supplies electrons, reduces the uncompensated spins of electrons in the 3d shell of nickel ions.

The downward slope of the Θ vs. z curve can be attributed to the fact that zinc ions mainly enter sublattice A and affect the exchange interaction in this sublattice. A reduction of the molecular-field constant α follows, accompanied by a reduction of Θ. It must be remembered that the constant C_N and the product $\lambda\mu$, which determine Θ, are also decreased as z increases. We can attempt to explain the increase of σ with z by assuming that the molecular-field constant n and thus the exchange interaction between sublattices increases with the number of zinc ions. It also follows from Néel's theory that σ, unlike the other constants, is quadratically dependent on n. In this connection it should be noted that, as Néel's calculations[5] for nickel-zinc ferrites have shown, the molecular field constant n has a tendency to increase with the amount of zinc oxide.

With an increase in the ZnO content $1/\chi_0$ decreases, but in a less complicated manner than Θ and C_N (Fig. 3).

Figure 4 shows the relation between $1/\chi$ and T for a few ferrites. The dashed curves were plotted from Néel's equation using the constants that had been obtained, while the solid curves were plotted from experimental data. At high temperatures the theoretical and experimental curves practically coincide. It should be noted especially that the agreement of the experimental and theoretical curves occurs for all ferrites of the nickel-zinc system although the shapes of the curves of $1/\chi$ as a function of T are extremely different. In all cases Néel's law is verified for ferrites over a broad temperature range, from approximately 850 to 1500°K. We must also note

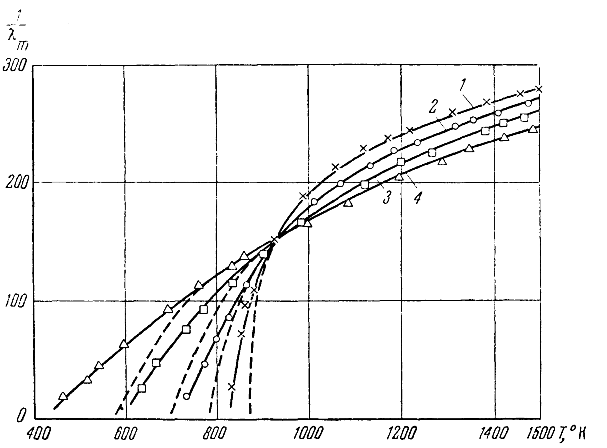

FIG. 4. Temperature dependence of the reciprocal susceptibility for the ferrites: 1 – $Fe_2O_3 \cdot 0.9NiO \cdot 0.1ZnO$; 2 – $Fe_2O_3 \cdot 0.7NiO \cdot 0.3ZnO$; 3 – $Fe_2O_3 \cdot 0.5NiO \cdot 0.5ZnO$; 4 – $Fe_2O_3 \cdot 0.3NiO \cdot 0.7ZnO$.

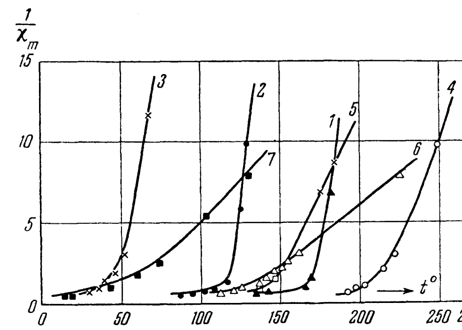

FIG. 5. Temperature dependence of the reciprocal susceptibility for ferrites. Temperature interval T = 650° + t° for 1 – $Fe_2O_3 \cdot 0.9\ NiO \cdot 0.1\ ZnO$, 2 – $Fe_2O_3 \times 0.8NiO \cdot 0.2ZnO$; 3 – $Fe_2O_3 \cdot 0.7NiO \cdot 0.3ZnO$; temperature interval T = 400° + t° for 4 $Fe_2O_3 \cdot 0.6NiO \cdot 0.4ZnO$, 5 – $Fe_2O_3 \cdot 0.5NiO \cdot 0.5ZnO$; temperature interval T = 300° + t° for 6 – $Fe_2O_3 \cdot 0.4NiO \cdot 0.6ZnO$, 7 – $Fe_2O_3 \cdot 0.3NiO \cdot 0.7ZnO$.

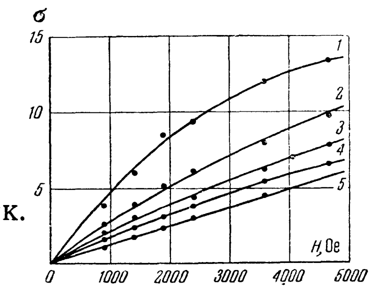

FIG. 6. Magnetization curves of the ferrite $Fe_2O_3 \cdot 0.5NiO \cdot 0.5ZnO$ at different temperatures: 1 – 537°, 2 – 547°, 3 – 550°, 4 – 553°, 5 – 556°K.

that near the ferromagnetic Curie point the theoretical and experimental curves do not agree and that this disagreement is most pronounced near Θ_f. We note that a similar behavior has been observed in pure ferrites such as Ni, Co, and Fe ferrites, according to Fallot and Maroni.[2] We believe that these discrepancies are caused to a considerable extent by the effect of short-range magnetic ordering especially in the immediate vicinity of the ferromagnetic Curie point. Inhomogeneity of the samples also probably contributes to the disagreement of theory and experiment.

3. To investigate the ferromagnetic transition region we measured the paramagnetic susceptibility at temperatures close to the ferromagnetic Curie point (Fig. 5). Very near Θ_f peculiar "tails" are seen, where the magnetic susceptibility depends on the magnetic field H as well as on temperature. Figure 6 shows a few isothermal magnetization curves (σ as a function of H) for one of the ferrites, where σ is the specific magnetization. Near Θ_f the magnetization curves are seen to be essentially linear; the departure from linearity increases as Θ_f is approached. At a sufficient distance from Θ_f the curves approximate straight lines and the paramagnetic susceptibility ceases to depend on the magnetic field. Similar behavior is observed in the other ferrites that were investigated.

An analysis of the experimental curves has shown that the dependence of σ on H near Θ_f can be represented analytically by

$$H = a\sigma + b\sigma^3, \tag{5}$$

where a and b are coefficients that depend on P and T.

In Fig. 6 Eq. (5) is represented by solid curves while the experimental values are given by dots. With suitably selected constants Eq. (5) is seen to give a satisfactory description of the experimental results. The experiments show that for all of the investigated ferrites the coefficient a increases linearly with temperature. The coefficient b is comparatively small and increases with temperature just as in the case of ferromagnetic metals.

In conclusion the authors wish to thank Professor E. I. Kondorskii and D. I. Volkov for their participation in a discussion of the results.

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Translated by I. Emin