SPECIFIC HEAT OF NICKEL-ZINC SYSTEM FERRITES IN THE LOW-TEMPERATURE REGION

M. O. KOSTRYUKOVA

Moscow State University

Submitted to JETP editor January 11, 1961

J. Exptl. Theoret. Phys. (U.S.S.R.) 40, 1638-1643 (June, 1961)

The magnetic contribution to the specific heat for the ferrites $NiFe_2O_4$, $ZnFe_2O_4$ and the mixture $0.2\,Ni \cdot 0.8\,ZnFe_2O_4$ is determined from calorimetric data obtained between 1.8 and 20° K.

IN this work the specific heats of the ferrites $NiFe_2O_4$, $ZnFe_2O_4$ and of the mixture of $0.2\,Ni \cdot 0.8\,ZnFe_2O_4$ have been measured in the temperature range from 1.8 to 20° K. The measured specific heats have been applied in elucidating the details of the magnetic energy spectrum of these substances.

The ferrites of the nickel-zinc system are suitable substances for this investigation, since for some of them the Curie temperature is sufficiently low, and one can therefore conclude that in the low temperature region the magnetic specific heat appreciably exceeds the specific heat due to the lattice vibrations.

It follows from neutron-diffraction data[1] and from the results of magnetic measurements,[2] that the so-called ferrimagnetic spin ordering takes place at $T_C \sim 870°$ K in nickel ferrite ($NiFe_2O_4$) and is preserved down to 20° K. In mixed ferrites the temperature of the transition to the state of magnetic ordering decreases with the increase in the concentration of the nonmagnetic zinc ions; according to Pauthenet,[2] magnetic ordering in the ferrite $0.2\,Ni \cdot 0.8\,ZnFe_2O_4$ occurs in the temperature range between 70 and 292° K. Yafet and Kittel[3] have discussed the picture of ordering in mixed ferrites and have, in particular, indicated the possibility of triangular spin ordering occurring in them. The results of the latest studies of the properties of zinc ferrite ($ZnFe_2O_4$)[4,5] indicate the occurrence of an antiferromagnetic transition in it at $T_C \sim 9.5°$ K.

Until recently, low temperature specific heat measurements were only available for one substance of the ferrite class — magnetite ($FeFe_2O_4$),[6] in which ferrimagnetic ordering takes place at a high temperature ($T_C = 843°$ K).

The ferrite specimens studied in this work had the spinel x-ray pattern without extra lines, and the accuracy of their stoichiometric composition, according to the chemical data and x-ray analysis, amounted to several per cent.*

The method described earlier[7,8] was used in the specific heat measurements. The surface of the specimens was covered with a thin film of BF varnish to reduce the possibility of adsorption of the exchange gas.

The values of the heat capacity of the ferrites $NiFe_2O_4$, $ZnFe_2O_4$ and of the mixture $0.2\,Ni \cdot 0.8\,ZnFe_2O_4$ between 1.8 and 20° K are shown in Fig. 1 in C-T coordinates.

It follows from the data presented that the specific heat of nickel ferrite ($NiFe_2O_4$) does not show any marked indication of an anomaly in its temperature dependence. In addition, the molar heat capacity of nickel ferrite is considerably lower than that of zinc or of the mixed ferrite, for which the anomalous specific heat is large.

Since the magnetic ordering in nickel ferrite occurs at a high temperature, one might expect that the magnetic contribution to the specific heat of $NiFe_2O_4$ at low temperatures should be small compared with the lattice specific heat.

Calculations, made according to formulae obtained on the basis of a semi-classical theory of spin waves, for ferrites with strong AB coupling[9,6] (the electron spins of the ions of the A and B sublattices are then oriented corresponding to the +Z and −Z directions) lead to the following values of the magnetic specific heat:

$$C_{mag} \approx 0.113R\{2(2S_B - S_A)kT/11J_{AB}S_AS_B\}^{3/2}$$

$$\approx 0.16 \cdot 10^{-4}T^{3/2} \text{ cal/mole-deg.}$$

$$kT_c \approx 4\sqrt{2}\,J_{AB}\sigma_A\sigma_B = 36.7J_{AB},$$

$$J_{AB} \approx 24.5k, \qquad \sigma_N^2 = S_N(S_N + 1).$$

*The ferrites were prepared by sintering in the Institute of Silicate Chemistry of the Academy of Sciences. The x-ray analysis of the specimens was kindly carried out by L. N. Rastorguev of the Steel Institute.

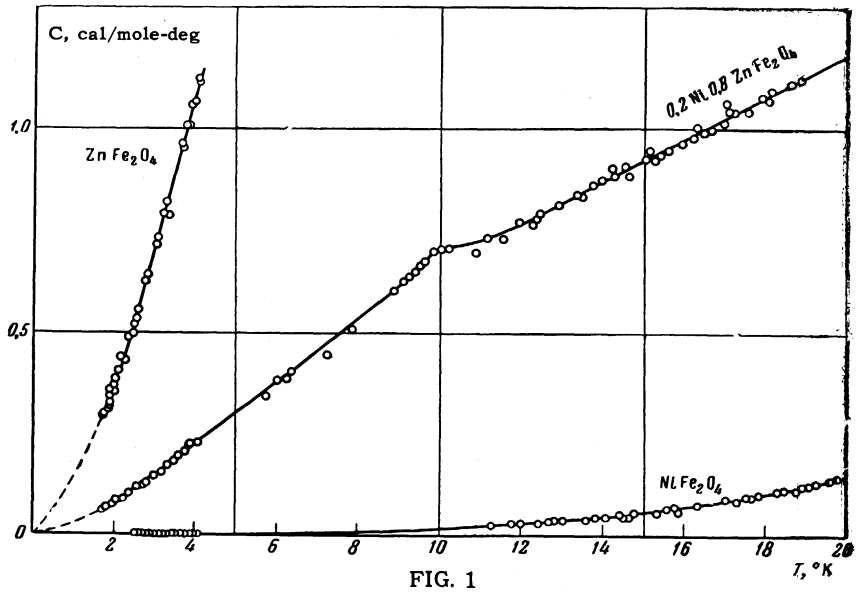

FIG. 1

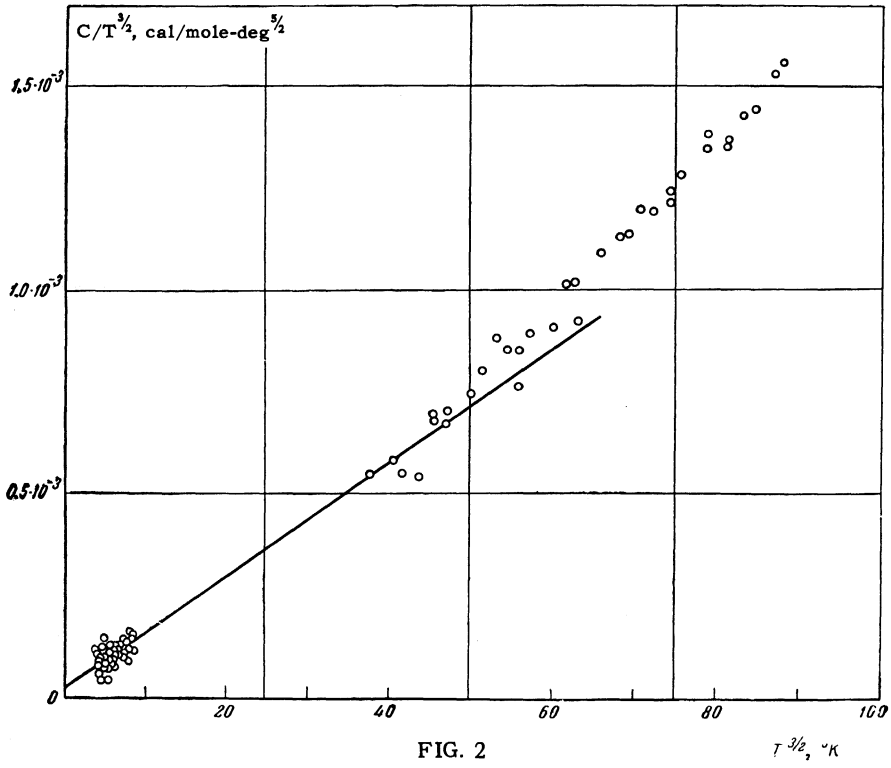

FIG. 2

Here S_A and S_B are the mean electron spins associated with the ionic moments of the tetrahedral and octahedral lattice sites, which for nickel ferrite are taken respectively as 1.75 and 2.5; J_{AB} is the negative exchange integral between nearest neighbor spins of the two sublattices. For the calculation, T_C is taken as 870° K.

In order to separate the magnetic specific heat from that due to the lattice vibrations, the results for nickel ferrite between 2 and 20° K are plotted in Fig. 2 as $C/T^{3/2}$ against $T^{3/2}$.* The straight line drawn through the experimental points corresponds to a specific heat between 2 and 12° K given by the expression

$$C[\text{cal/mole-deg.}] = 0.14\cdot10^{-4}T^3 + 0.16\cdot10^{-4}T^{7/2},$$

where the cubic term naturally describes the lattice specific heat ($\Theta_D = 321°$ K) and the term proportional to $T^{3/2}$ the magnetic specific heat.

We can thus consider that the experimental data for nickel ferrite do not contradict the results of the calculation, and the magnetic specific heat between 2 and 20° K represents a small fraction of the lattice specific heat. In what follows, the esti-

*More detailed data on the specific heat of $NiFe_2O_4$ are given elsewhere.[10]

mate of the specific heat corresponding to the lattice vibrations of zinc and of the mixed ferrites has been made according to the data obtained for nickel ferrite.

It should be noted that our data on the lattice specific heat of $NiFe_2O_4$ are close to the lattice specific heat of magnetite ($FeFe_2O_4$),[6] for which $C_{lattice} = 0.112 \times 10^{-4} T^3$ cal/mole-deg. However, the magnetic specific heat of magnetite, proportional to $T^{3/2}$ (see reference 6), is roughly 20 times greater than the magnetic contribution to the specific heat of $NiFe_2O_4$. It is possible that this is connected with the existence of the α-β transition in magnetite at 113° K.[11]

An anomaly was found in the C-T curve (Fig. 1) for the mixed nickel-zinc ferrite $0.2\,Ni \cdot 0.8\,ZnFe_2O_4$, with a maximum at a temperature ~ 9.7° K. An analogous anomaly in specific heat was found in mixed nickel-zinc ferrites by Westrum and Grimes,[12] and is probably connected with the antiferromagnetic transition in zinc ferrite at ~ 9.5° K.[4,5]

From the data shown in Fig. 3, where the coordinates are $C/T^{3/2}$ and $T^{3/2}$, it follows that the specific heat of the ferrite $0.2\,Ni \cdot 0.8\,ZnFe_2O_4$ can be represented by the following formula between 1.8 and 4° K:

$$C[\text{cal/mole-deg.}] = 4{,}5 \cdot 10^{-4} T^3 + 2{,}5 \cdot 10^{-2} T^{3/2}.$$

The cubic term separated out in this way cannot, however, be ascribed solely to the lattice specific heat, since for nickel ferrite the lattice specific heat is 32 times smaller than the cubic term in the specific heat of the mixed nickel-zinc ferrite.

The term in the heat capacity of the ferrite $0.2\,Ni \cdot 0.8\,ZnFe_2O_4$ which is proportional to $T^{3/2}$ exceeds the cubic term over a large part of the range of measurements (up to 14° K). Between 4 and 9.7° K the experimental data are close to the value of the term proportional to $T^{3/2}$, while above 9.7° K the growth in specific heat is considerably slowed down.

We can, therefore, consider that an appreciable part of the magnetic specific heat between 1.8 and 4° K is connected with the ordering which takes place below 9.7° K in the mixed nickel-zinc ferrite.

It is also seen from the data that the magnetic specific heat of the mixed nickel-zinc ferrite continues to increase with increasing temperature between 9.7 and 20° K (Fig. 1). This indicates that magnetic ordering in the mixed ferrite is preserved at higher temperatures and that the specific heat has a maximum lying above 20° K.

The maximum in the specific heat of the zinc ferrite we measured was found at 9.5° K; at this temperature the value is of the order of 3.5 cal/mole-deg. The experimental data shown in Fig. 4 for temperatures between 1.8 and 4° K, in $C/T^{3/2}$ and $T^{3/2}$ coordinates, enable one to express the specific heat by the relation

$$C[\text{cal/mole-deg.}] = 1.8 \cdot 10^{-3} T^3 + 12.1 \cdot 10^{-2} T^{3/2}.$$

The cubic term in the specific heat of zinc ferrite exceeds appreciably both the lattice specific heat of nickel ferrite (by 130 times) and the cubic contribution to the specific heat of the mixed nickel-zinc ferrite (by 4 times).

The $T^{3/2}$ term in the specific heat of nickel ferrite is 4.8 times greater than the $T^{3/2}$ term in the mixed ferrite.

The absence of a complete theory describing the state of magnetic ordering in zinc ferrite and in mixed nickel-zinc ferrites makes a comparison of the experimental data with theory difficult. The energy spectrum of antiferromagnets predicted by theory leads to a cubic temperature dependence of the magnetic specific heat in the region of not too low temperatures[13] (for temperatures greater than the gap in the energy spectrum of the antiferromagnet) and cannot explain the $T^{3/2}$ law.

At the same time, bearing in mind the fact that the $T^{3/2}$ term in the magnetic specific heat is large in zinc ferrite, we might think that both the cubic term and the $T^{3/2}$ term in the magnetic specific heat are due to antiferromagnetic ordering in $ZnFe_2O_4$.

In the process of preparation, zinc ferrite is always partly inverted.[2,14] A certain fraction of

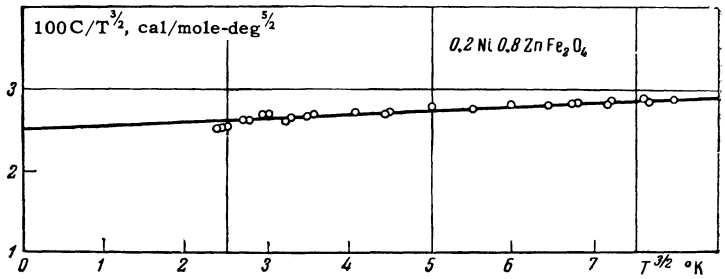

FIG. 3

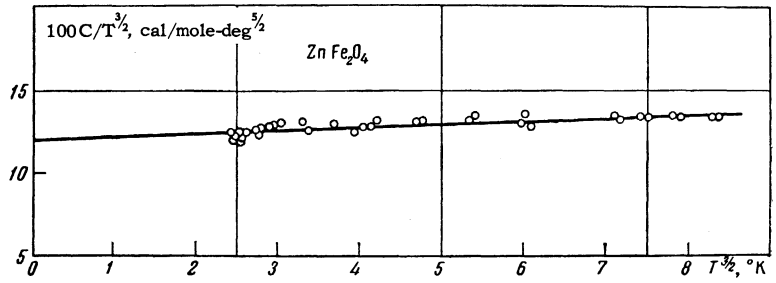

FIG. 4

the Zn ions of the A sublattice then changes place with the Fe ions of the B sublattice. The magnetic ordering may then be more complicated than, for example, the triangular type suggested by Yafet and Kittel[3] for mixed nickel-zinc ferrites with small Ni concentration.

It is highly likely that a considerable part of the $T^{3/2}$ specific heat is connected with this more complicated form of magnetic ordering, which takes place at low temperatures in different regions of a zinc ferrite specimen. The maximum specific heat at $\sim 9.7°$ K in the mixed nickel-ferrite $0.2\,Ni \cdot 0.8\,ZnFe_2O_4$ is possibly produced by inclusions of the zinc ferrite type.

In conclusion, I express my sincere thanks to A. I. Shal'nikov for his constant interest in the work, to A. S. Borovik-Romanov, who took part in the discussion of the results, and to E. F. Gippius for help with the experiments.

[1] J. M. Hastings and L. M. Corliss, Revs. Modern Phys. **25**, 114 (1953).

[2] R. Pauthenet, Ann. de Phys. **7**, 710 (1952).

[3] Y. Yafet and C. Kittel, Phys. Rev. **87**, 290 (1952).

[4] J. M. Hastings and L. M. Corliss, Phys. Rev. **102**, 1460 (1956).

[5] E. F. Westrum, Jr. and D. M. Grimes, J. Phys. Chem. Solids **3**, 44 (1957).

[6] J. S. Kouvel, Phys. Rev. **102**, 1489 (1956).

[7] M. O. Kostryukova, Doklady Akad. Nauk SSSR **96**, 959 (1954).

[8] M. O. Kostryukova, JETP **30**, 1162 (1956), Soviet Phys. JETP **3**, 771 (1956).

[9] H. Kaplan, Phys. Rev. **86**, 121 (1952).

[10] M. O. Kostryukova and T. A. Leĭstner Вестник МГУ (Moscow State University Bulletin) **4** (1961).

[11] S. V. Vonsovskii, Современное учение о магнетизме (Modern Theories of Magnetism) part III, Gostekhizdat, 1953, Sec. 13.

[12] E. F. Westrum Jr. and D. M. Grimes, J. Phys. Chem. **61**, 761 (1957).

[13] Akhiezer, Bar'yakhtar, and Kaganov, Usp. Fiz. Nauk **71**, 533 (1960), Soviet Phys. Uspekhi **3**, 567 (1961).

[14] E. F. Westrum Jr. and D. M. Grimes, J. Phys. Chem. Solids **6**, 280 (1958).

Translated by R. Berman
280