SOVIET PHYSICS JETP VOLUME 34, NUMBER 3 MARCH, 1972

TEMPERATURE DEPENDENCE OF THE PARAMAGNETIC SUSCEPTIBILITY OF INDIUM-SUBSTITUTED M-TYPE FERRITES

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Submitted February 22, 1971

Zh. Eksp. Teor. Fiz. 61, 1073—1077 (September, 1971)

An investigation was made of the temperature dependence of the paramagnetic susceptibility of the indium-substituted ferrites $BaOFe_{12-x}In_xO_{18}$ with $0 \leq x \leq 1.6$. It was found that the molecular field coefficients of these ferrites could be determined from the temperature dependences of the reciprocal susceptibility above the Curie point by the application of Néel's two-sublattice model. It was possible to apply this model by selecting the sublattices in the following way: sublattice A – $4f_1$, $4f_2$ ions; sublattice B – 2a, 2b, 12k ions. The molecular field coefficients α and β, corresponding to the $\alpha-\beta$ diagram—to the experimentally observed temperature dependences of the saturation magnetization $\sigma_s(T)$, were determined for all the investigated ferrites which had different types of $\sigma_s(T)$ curve. A transition from the Q- to the P-type of $\sigma_s(T)$ curve resulted in an increase in the intrasublattice AA interaction (α), whereas the BB interaction was practically unaffected (β).

THE present paper describes an investigation of the temperature dependence of the paramagnetic susceptibility of the hexagonal indium-substituted M-type ferrites $BaOFe_{12-x}In_xO_{18}$ with the following concentrations of In^{3+} ions: x = 0.2, 0.4, 0.6, 0.8, 1.2, and 1.6. The results obtained were used to calculate the molecular field coefficients α and β. The calculations were based on Néel's two-sublattice model. Till now such calculations have been carried out mainly for spinel structures. The molecular field coefficients for unsubstituted M-type ferrites and for mixed W-type Ferroxplanas were calculated in[1], and those for ferrite garnets in[2].

The selection of In^{3+} as the substituent ion was considered in[3]. The selected system was interesting because, beginning from certain concentrations of In^{3+}, the temperature dependences of the saturation magnetization were of the "humped" type. This was due to the considerable changes which took place in the intrasublattice exchange interactions (or one of them) and which finally gave rise either to a noncollinear spin structure or simply to a change in the temperature dependence of the sublattice magnetizations (Néel's P- and N-types).[4-6]

Investigations of the Mössbauer effect have established that M-type ferrites have a five-sublattice magnetic structure.[7,8] However, if the structure is considered on the basis of Gorter's geometrical scheme for indirect exchange,[9] one can combine the 2a, 2b, and 12k sublattices into one, which we shall call the B sublattice (eight magnetic ions), and the $4f_1$ and $4f_2$ sublattices into another sublattice, which we shall call A (four magnetic ions). The selection is made in such a way that the B sublattice is dominated by the interaction between the octahedral ions at the boundary of the R block and the ions in the octahedra of the S blocks. The interaction between the other ions is weaker because the distances between them are greater. The A sublattice is dominated by the interaction between the $4f_2$ ions. Thus, the exchange interactions within the sublattices can be reduced to interactions between pairs of ions. In this scheme, the spins of the ions within each sublattice are directed parallel to one another. The net sublattice magnetizations are antiparallel. The strongest exchange interaction is that between the sublattices, whereas within each sublattice this interaction is considerably weaker.

Néel's theory can now be applied because the investigated ferrites may be regarded as consisting of two sublattices each. This is acceptable because there is only one type of magnetic ion (Fe^{3+}) and because the degree of dilution with nonmagnetic ions is small (13%).

1. PREPARATION OF SAMPLES, MEASUREMENT METHOD, AND CALCULATIONS

Polycrystalline samples were prepared by the usual ceramic technique. The firing temperature was 1250—1300° C. This temperature was applied for 10—20 h. The single-phase nature of all the samples was checked by a metallographic method; some samples were investigated by x-ray diffraction.

The temperature dependences of the paramagnetic susceptibility were determined by the Gouy method, using samples whose dimensions were 55 × 2 × 2 mm. These dependences were obtained between the Curie points and 1000°C, in fields up to 7 kOe. The experimental error was 1%. No correction was made for the diamagnetism.

The molecular field coefficients were calculated by the method described in[2]. The parameters Θ, σ, and $1/\kappa_0$, occurring in Néel's equation for the temperature dependence of the reciprocal paramagnetic susceptibility,[4] were calculated from the experimental dependences $1/\kappa = f(T)$ and are listed in Table I. The theoretical curves $1/\kappa_{theor} = f(T)$, plotted on the basis of these parameters, agreed with the experimental dependences over a wide range of temperatures with the exception of the regions near the Curie points. This discrepancy was probably due to the presence of short-range order. Table I gives the values of the paramagnetic Curie

Table I. Parameters Θ, σ, and $1/\kappa_0$—calculated from dependences $1/\kappa = f(T)$—and paramagnetic Curie points Θ_p deduced from theoretical curves

Composition	Θ, °K	$\sigma \cdot 10^{-3}$	$1/\kappa_0$	Θ_p, °C	Composition	Θ, °K	$\sigma \cdot 10^{-3}$	$1/\kappa_0$	Θ_p, °C
M	830	5.9	46	515	$M\,In_{0.8}$	520	10.8	46	395
$M\,In_{0.2}$	795	6.18	45	510	$M\,In_{1.2}$	276	19.3	51	330
$M\,In_{0.4}$	720	6.3	43	460	$M\,In_{1.6}$	280	15.5	46	250
$M\,In_{0.6}$	492	12.2	47	435					

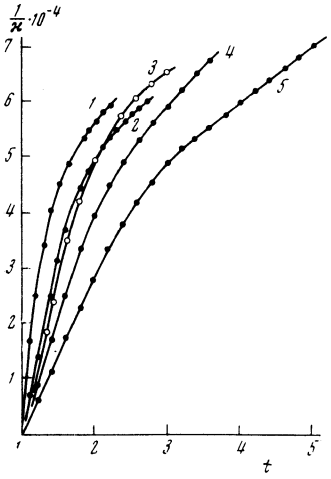

FIG. 1. Dependences of the reciprocal susceptibility on the reduced temperature $1/\kappa = f(t)$, where $t = T/T_C$, for indium-substituted ferrites: 1) x = 0; 2) x = 0.4; 3) x = 0.8; 4) x = 1.2; 5) x = 1.6.

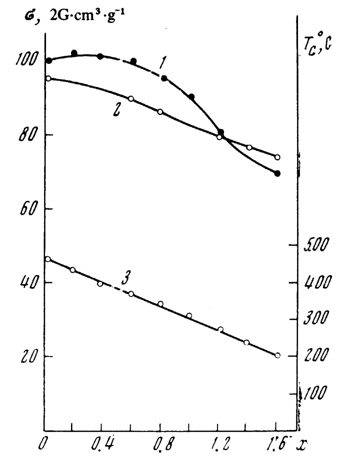

FIG. 2. Dependences of the saturation magnetization at 4.2°K (curve 1) and at 77°K (curve 2) on the concentration of indium ($0 \leqslant x \leqslant 1.6$) in indium-substituted ferrites. Curve 3 represents the concentration dependence of the Curie point.

points Θ_p, deduced from the theoretical dependences $1/\kappa_{theor} = f(T)$.

2. EXPERIMENTAL AND CALCULATED DATA. DISCUSSION OF RESULTS

Figure 1 shows the dependences of the reciprocal susceptibility on the reduced temperature: $1/\kappa = f(T, °C/T_C, °C)$. It is evident from Fig. 1 that the nature of these curves changes with increasing concentration of In^{3+}.

Figure 2 presents the concentration dependences of the specific saturation magnetization at 4°K (curve 1) and at 77°K (curve 2), and of the ferromagnetic Curie point T_C (curve 3). The errors in these measurements were, respectively, 1, 3, and 1%. It is evident from Fig. 2 that "humped" curves appeared beginning from the In^{3+} concentration x = 1.2. The Curie points of the investigated materials decreased linearly from 460°C for the barium ferrite to 200°C for the material with x = 1.6.

Table II gives the values of the molecular field coefficients α and β. The numbers of the iron ions in the A and B sublattices (λ and μ) were calculated from the saturation magnetization σ_s at 4.2°K. The temperature coefficients γ were, as in[2], negative and ranged from -2.14×10^{-4} to -0.3×10^{-4}, decreasing with increasing concentration of In^{3+}. It is evident from Table II that an increase in the number of the substituent In^{3+} ions resulted in an increase in α, which remained negative, whereas β decreased (or remained constant within the limits of the experimental error). This can be explained by a change in the geometry of the exchange interaction structure because the interplanar distances (the lattice constants[3]) increased with increasing concentration of indium. A large fraction of the substituent indium ions in the materials with x = 1.2 and x = 1.6 (Table II) was located in the B sublattice and this of itself should reduce the coefficients β. However, bearing in mind the change in the geometry of the structure, we may expect this reduction to be small.

Table II. Number of Fe^{3+} ions in A and B sublattices (λ and μ, respectively) and molecular field coefficients of A and B sublattices (α and β, respectively)

Composition	λ	μ	α	β
M	4.000	8.00	-0.67 ± 0.03	-0.34 ± 0.02
$M\,In_{0,2}$	3.85	7.95	-0.66 ± 0.02	-0.32 ± 0.01
$M\,In_{0,4}$	3.78	7.82	-0.7 ± 0.05	-0.30 ± 0.02
$M\,In_{0,6}$	3.70	7.70	-1.05 ± 0.05	-0.31 ± 0.01
$M\,In_{0,8}$	3.62	7.58	-1.03 ± 0.05	-0.27 ± 0.03
$M\,In_{1,2}$	3.74	7.06	-1.38 ± 0.05	-0.26 ± 0.02
$M\,In_{1,6}$	3.73	6.67	-1.34 ± 0.05	-0.24 ± 0.03

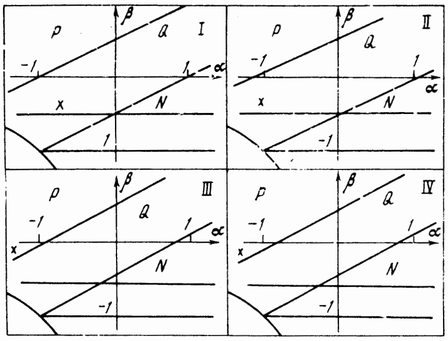

FIG. 3. Neel's diagrams for indium-substituted ferrites: I) x = 0; II) x = 0.8; III) x = 1.2; IV) x = 1.6.

Néel's diagrams for the compositions with x = 0, 0.8, 1.2, and 1.6 are plotted in Fig. 3. It follows from these diagrams that the composition with x = 1.2 represents the limit for the Q-P transition. The values of α and β for the compositions with x = 1.2 and x = 1.6 lie in that part of Néel's diagram which corresponds to the P-type temperature dependence of the magnetization, in agreement with the results presented in Fig. 2.

Thus, the following conclusions can be drawn from the results obtained.

1. A qualitative description of the exchange interaction in M-type hexaferrites can be given on the basis of Néel's two-sublattice model. This is confirmed by the agreement between the experimental and the theoretical temperature dependences of the reciprocal susceptibility $1/\kappa = f(T)$, as well as by the fact that the values obtained for α and β correspond, in Néel's $\alpha-\beta$ diagram, to the type of the temperature dependence of the magnetization $\sigma_s(T)$ observed experimentally.

2. The substitution of Fe^{3+} ions with nonmagnetic In^{3+} ions affects strongly (even in the case of indium concentrations up to 13%) the exchange interaction: a transition occurs from the Q- to the P-type temperature dependence of the magnetization and the Curie point falls significantly. The replacement of Fe^{3+} with In^{3+} ions enhances the interaction in the A sublattice (α) and weakens slightly the interaction in the B sublattice (β). This strong influence of indium ions is due to the large change in the geometry of the structure because there is obviously no breaking of the exchange bonds.

The question whether the approach described here can be used to study noncollinear structures remains open. The existence of noncollinear structures in indium-substituted M-type ferrites with indium concentrations $x \geq 1.9$ has been demonstrated in[6]. The range of concentrations x = 1.2–1.9 has not yet been investigated. A sample with x = 1.2 shows no singularities typical of noncollinear structures, and the dependence $\sigma_s(T)$ is of the Q-type in the range $T \geq 77°K$. Our study shows that this composition represents the limit at which a transition from the Q- to the P-type dependence takes place. It must also be mentioned that the cation distribution in the samples that we investigated is different from that in the samples used in[6], as indicated (for example) by the concentration dependences of the Curie points.

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Translated by A. Tybulewicz
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