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EFFECT OF IONIC ORDERING ON THE MAGNETOSTRICTION OF LITHIUM FERRITE

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The effect of ionic ordering on the magnetostriction of lithium ferrite is investigated. Measurements of the magnetostriction constants λ_{100} and λ_{111} were made by the method of ferromagnetic resonance in the temperature range from −170 to +340°C. The results of the measurements show a strong effect of the degree of ordering of the ions upon the magnetostriction. A compensation point of the magnetostriction constant λ_{111} was detected for disordered lithium ferrite at a temperature of about 160°C. The experimental data are interpreted on the basis of Callen's theory of the magnetostriction of cubic ferrimagnets.

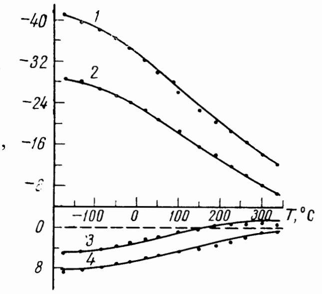
LITHIUM ferrite $Li_{0.5}Fe_{2.5}O_4$, which has the inverse spinel structure, can exist in states with different degrees of ionic ordering of the cations on octahedral sites, depending on its previous thermal history[1-4]. The transition to an ordered state occurs at a temperature of about 750°C and, according to[3], occupies a temperature interval of the order of 50°C. The temperature of the "order-disorder" transition in general depends on the composition of the lithium ferrite. In the ordering process, three iron ions Fe^{3+} and one lithium ion are arranged successively along directions of the [100] type; that is, in the ordered lithium spinel each row of octahedral ions in a direction of the [100] type contains a Li^+ ion in every fourth site. This is the so-called 3 : 1 type of long-range order of B-ions. In such ordering, each Li^+ ion is surrounded by an octahedron of six Fe^{3+} ions, stretched out along a trigonal axis, and each Fe^{3+} ion is surrounded by four Fe^{3+} ions and two Li^+ ions. The space groups of ordered and disordered lithium ferrite are, respectively, $O(6) - P4_33$ (or $P4_13$) and $O_h(7) - Fd3m$.

The capacity of lithium ferrite to be in different states of ionic ordering is of great interest from the point of view of a study of the microscopic nature of the magnetism of ferrites. The effect of ionic ordering on the magnetocrystalline anisotropy energy was studied by Folen[5]. It was found that the first anisotropy constant of disordered lithium ferrite was appreciably larger in absolute value than the corresponding constant of ordered lithium ferrite. Interpretation of this effect, within the framework of the one-ion theory of crystallographic anisotropy[6,7], led Folen[5] to the deduction that the change in question cannot be explained by any admissible change of the coefficients of splitting of the spin multiplet of the Fe^{3+} ion by a crystalline field of cubic symmetry. Evidently an essential role is played by deformations of axial symmetry, which change as a result of the "order-disorder" transition.

Investigation of the electron paramagnetic resonance spectrum of the Cr^{3+} ion in the ordered lithium-aluminum spinel $Li_{0.5}Al_{2.5}O_4$[8] showed the presence of a rhombic distortion of the crystalline field on the octahedral sites. A rhombic distortion arises as a result of the fact that of the six nearest cation neighbors of an Fe^{3+} ion in an octahedral position, as has already been pointed out above, two are Li^+ ions. It is natural that the effect of a rhombic distortion of the crystalline field should depend considerably on the state of cation ordering on the octahedral positions of lithium ferrite, and consequently the latter, through the mechanism of rhombic distortion, can have a marked effect on the structure-sensitive properties of the material, such for example as the crystallographic anisotropy and the magnetostriction.

It can be expected that the magnetostriction of lithium ferrite will be peculiarly sensitive to a change of the degree of ionic ordering, since in the case of a cubic crystal, whose magnetic ions are in S-states, the magnetostrictive mechanism connected with axial and rhombic distortions can be important.

On the basis of this supposition, we carried out an investigation of the effect of ionic ordering on the magnetostriction of lithium ferrite. The measurements were made on spherical specimens of lithium ferrite single crystals, grown in a state of complete order by the method of Remeika and Comstock[9] in the Institute of Physics of the Siberian Division, Academy of Sciences, U.S.S.R., by V. N. Seleznev. All the original reagents used in the growing of the crystals were of grade OSCh (special purity) and SPCh (spectrographic purity). In this respect the specimens investigated here differ from the specimens on which the temperature dependence of the magnetostriction of lithium ferrite was studied by us earlier[10]. The magnetostriction measurements were made by the ferromagnetic-resonance method, by the procedure described earlier[10,11]. The ferrite pellets had a diameter of the order of 1 mm.



Temperature dependence of the magnetostriction constants of a single crystal of lithium ferrite (points, experiment; continuous curve, theory). Curves 1 and 3 describe λ_{100} and λ_{111}, respectively, for disordered lithium ferrite; curves 2 and 4 describe λ_{100} and λ_{111}, respectively, for ordered lithium ferrite.

In order to check the effect of plastic surface deformations, which arise during the manufacture of the pellets, on the results of the measurements, a preliminary investigation was made of the effect of annealing. For this purpose, measurements of the magnetostriction constants λ_{100} and λ_{111} were made initially on the unannealed specimens immediately after mechanical working, and then, to relieve the stresses, the specimen was annealed according to the method proposed by Schnitzler, Folen, and Rado[12]. Measurements of the constants λ_{100} and λ_{111} made after such annealing did not disclose any appreciable change of magnetostriction. Therefore we did not thereafter perform a similar heat treatment of the specimens under study.

In the figure, the results of measurements of the magnetostriction constants λ_{100} and λ_{111}, on one of the specimens investigated in the ordered state, are shown by points. The magnetostriction constants λ_{100} and λ_{111} have different signs, and both decrease monotonically in absolute value on increase of the temperature from -170 to $+340$°C, nowhere becoming zero. The constant $|\lambda_{100}|$ appreciably exceeds the value of $|\lambda_{111}|$. It is interesting to note that the constant λ_{111}, in contrast to results obtained earlier[10] for lithium ferrite grown by another technique, has a positive sign. We think that this difference is connected with the use in the present work of crystals of greater "purity," and also with the complete ordering of their structure. This is confirmed by chemical analysis of the crystals used here and of the crystals used in[10]. The latter have, for example, a noticeable admixture of Co^{2+} (0.1–0.4%). The crystals investigated in the present work contain no admixtures of Co^{2+} or Fe^{2+}.

In the same figure are shown the results of measurements of the magnetostriction for the same specimen in the disordered state. It is easy to see that $|\lambda_{100}|$ of disordered lithium ferrite is about 1.5 times larger than $|\lambda_{100}|$ of the ordered ferrite. The qualitative character of the temperature dependence of the constant λ_{100} remains similar to that obtained for ordered lithium ferrite. On the other hand, the magnetostriction constant λ_{111}, on transition of the lithium ferrite to the disordered state, diminishes greatly and shows a compensation point at a temperature of about 160°C. At this point, λ_{111} changes sign. This interesting experimental result confirms a prediction of theory[13] concerning the possibility of the existence, in two-sublattice ferrites, of a compensation point of the magnetostriction without compensation of the magnetization. On further increase of temperature, the constant $|\lambda_{111}|$ initially increases, reaches a maximum in the neighborhood of 270°C, and then begins to decrease smoothly up to 370°C.

The disordered state of the lithium ferrite was produced by heating the specimen, in a quartz ampoule, to 1000°C and then cooling the ampoule with the specimen in water. In general there is no basis for considering, on the basis of these measurements alone, that the above-described effect of such heat treatment of the specimen is determined wholly or even chiefly by a transition of the ferrite into a disordered state. Therefore we undertook the following additional investigations. The initially quenched specimen, for relief of the stresses engendered by the quenching, was subjected to an anneal at a temperature of about 650°C for a period of two hours and was subsequently cooled to 300°C at the rate of 1°C per minute. Measurements of λ_{100} and λ_{111} were then made. It was found that such annealing gave no appreciable effect. Then the same specimen was restored to the ordered state by heating it to 800°C, holding it at that temperature for two hours, then lowering the temperature at 1.5°C per minute to 600°C, holding it at that temperature for an hour, and finally cooling it to 300°C at the rate of 1°C per minute. Subsequent magnetostriction measurements showed that the results practically coincided with the original results, obtained on the ordered crystal; that is, this heat treatment transformed curves 1 and 3 in the figure to curves 2 and 4 respectively.

Repetition of the whole series of measurements on this specimen, as well as on another specimen obtained from a single crystal of the same batch, gave identical results. For comparison, we made measurements of the magnetostriction constants of a single crystal of yttrium ferrite before and after quenching it from 1000°C. These measurements showed an absence of any appreciable effect of such heat treatment on the magnetostriction of yttrium ferrite. Thus we conclude that the stresses produced by quenching of a ferrite from 1000°C show no important influence on measured values of the magnetostriction constants. In addition to this, the lack of dependence of the magnetization of lithium ferrite upon the "order-disorder" transition is evidence that redistributions of the cations do not occur on passage from the ordered state to the disordered and vice versa. All of this allows us to consider that the observed change of the magnetostriction of lithium ferrite that occurs on quenching of it from 1000°C is determined chiefly by a transition of the crystal into a disordered state.

Measurements of the anisotropy constant K_1 of ordered and disordered lithium ferrite, made by us, confirm the results of Folen's investigations[5].

We have interpreted the results obtained, on the basis of the theory of the magnetostriction of cubic ferrimagnets developed by Callen et al.[13] According to this theory, the temperature dependences of the magnetostriction constants λ_{100} and λ_{111} can be described by the relations

$$\begin{aligned}\lambda_{100} &= \frac{1}{c_{11}-c_{12}}\frac{5}{\sqrt{4\pi}}\sum_n B^{\gamma}_{0,2}(n)\, I_{5/2}[L^{-1}(m_n)],\\ \lambda_{111} &= \frac{1}{3c_{44}}\left(\frac{15}{4\pi}\right)^{1/2}\sum_n B^{\varepsilon}_{0,2}(n)\, I_{5/2}[L^{-1}(m_n)],\end{aligned} \tag{1}$$

where $B^{i}_{0,2}(n)$ are magnetoelastic coupling coefficients of the n-th sublattice, $I_{5/2}$ is a hyperbolic Bessel function, L^{-1} is the inverse Langevin function, m_n is the temperature-dependent magnetization of the n-th lattice, and c_{11}, c_{12}, and c_{44} are the elastic constants.

The magnetoelastic coupling coefficients that enter into the relations (1) were so chosen as to guarantee an acceptable agreement of the calculated and experimental temperature dependences of the magnetostriction constants. This requires knowledge of the temperature dependences of the sublattice magnetizations and of the elastic constants of lithium ferrite. We found in the literature no data on the temperature dependence of the elastic constants, and no investigations of the effect of the "order-disorder" transition on the elastic constants and the sublattice magnetizations. In this connection we supposed that the elastic constants of lithium ferrite do not depend on the degree of ionic ordering or on the temperature and that the sublattice magnetizations do not depend on the degree of ionic ordering. Evidently such a supposition leads to no significant error: first, because the elastic constants are only weak functions of temperature; and second, because no effect of the degree of ionic ordering on the magnetization of lithium ferrite has been noted.

The values of the elastic constants were taken from the paper of Comstock and Nilsen[14]; the lithium ferrite crystal was considered to be elastically isotropic. The temperature dependences of the sublattice magnetizations of a single crystal of ordered lithium ferrite, measured by the neutron-diffraction method, were described by Prince[15]. With use of these data, the following values were found for the magnetoelastic coupling coefficients: for ordered lithium ferrite,

$$\overset{\gamma}{B}_{0,2}(A) = 59 \cdot 10^6 \text{ erg} \cdot \text{cm}^{-3} \qquad \overset{\varepsilon}{B}_{0,2}(A) = -53 \cdot 10^6 \text{ erg} \cdot \text{cm}^{-3}$$

$$B^{\gamma}_{0,2}(B) = -88.7 \cdot 10^6 \text{ erg} \cdot \text{cm}^{-3} \qquad B^{\varepsilon}_{0,2}(B) = 70.5 \cdot 10^6 \text{ erg} \cdot \text{cm}^{-3}$$

and for disordered,

$$B^{\gamma}_{0,2}(A) = 63{,}9 \cdot 10^6 \text{ erg} \cdot \text{cm}^{-3} \qquad B^{\varepsilon}_{0,2}(A) = -60.2 \cdot 10^6 \text{ erg} \cdot \text{cm}^{-3}$$

$$B^{\gamma}_{0,2}(B) = -105.7 \cdot 10^6 \text{ erg} \cdot \text{cm}^{-3} \qquad B^{\varepsilon}_{0,2}(B) = 71.2 \cdot 10^6 \text{ erg} \cdot \text{cm}^{-3}$$

Substitution of the coefficients (2) and (3) into the relations (1) leads to the dependences shown in the figure by the continuous curves. Although the agreement of the calculated and experimental temperature dependences is good, it should be mentioned that in the choice of the magnetoelastic coupling coefficients of disordered lithium ferrite there is a considerable arbitrariness, inasmuch as the agreement of theory with experiment in this case is incomplete.

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