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VARIATION OF MAGNETOSTRICTION IN HEAT-TREATED COBALT FERRITE

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The magnetic field dependence of magnetostriction λ is determined in cobalt ferrite after quenching from different temperatures. The anomalous increase of $|\lambda_s|$ in samples quenched from temperatures below the Curie point can be accounted for by assuming that oxygen is dissolved in the ferrite lattice. The smaller lattice constant observed in the same temperature range is consistent with this assumption.

1. Uncertainty still characterizes our knowledge of magnetostriction in ferrites. Large discrepancies are often found between measurements reported by different authors who had investigated ferrites of the same composition. For example, in the case of cobalt ferrite values of the saturation longitudinal magnetostriction λ_s differ by almost 100% ($\lambda_s = -110 \times 10^{-6}$ in [1] and -210×10^{-6} in [2]). This wide disagreement cannot be accounted for by the influence of uncontrollable impurities in the materials used to prepare the ferrites, but evidently depends on the character of the heat treatment to which the ferrite was subjected.

In [3] a low value of λ_s was reported for cobalt ferrite prepared by annealing and baking in a neutral (nitrogen) atmosphere. When this ferrite was subsequently annealed in air at a lower temperature excess (non-stoichiometric) oxygen was dissolved in it, accompanied by an increase of λ_s.

Heating to high temperatures can lead to the partial dissociation of a ferrite because its components have different vapor pressures. When a ferrite is cooled very rapidly it can remain partially or completely fixed in its high-temperature state. At high temperatures, when intensive diffusion processes develop, the strict (normal or inverse) tetrahedral and octahedral ordering of the ions can be disrupted.[4] This represents an increase of entropy which is brought about with the aid of thermal fluctuations. The foregoing phenomena will induce changes in the magnetic properties of a ferrite, particularly in its magnetostriction. In the present work the magnetostriction of $CoFe_2O_4$ has been investigated by varying the heat treatment in order to elucidate the large spread of the values of λ.

2. Samples of cobalt ferrite were prepared from analytically pure Co_2O_3 and Fe_2O_3 powders, employing the customary ceramic technology described in [3]. To facilitate the interaction of the ferrite with the external air, highly porous samples were desirable (40—50% porosity, with $\sim 5\,\mu$ pores and 2—3 g/cm^3 density). For this reason the powders were subjected to a relatively low pressure of 60 kg/cm^2.

In order to fix the state of the ferrite after heating to a high temperature, the samples were quenched from different temperatures either by quick immersion in water or by transfer to a copper ampoule cooled by flowing water. Most water-quenched samples cracked and were unsuitable for further work. However, it was possible to ascertain that close values of the magnetostriction were obtained for samples quenched from the same temperature by both methods. The measurements that are to be reported here were obtained with samples quenched by rapid transfer into the ampoule. Longitudinal and transverse magnetostriction were measured tensometrically at room temperature.

3. Samples quenched from different temperatures (at intervals of 100° beginning at 1200°C or lower) were used to determine the longitudinal $\lambda_{\parallel}$ and transverse $\lambda_{\perp}$ magnetostriction as functions of the magnetic field. In almost all quenched samples $\lambda_{\parallel}$ in a 10^4 Oe field was lower than in a sample that was cooled slowly to room temperature. Also, for samples quenched from high temperatures in high fields we obtained $d\lambda_{\parallel}/dH = d\lambda_{\perp}/dH > 0$. This may indicate that considerable positive volume magnetostriction λ_p due to the "paraprocess" was superimposed on the linear magnetostriction λ.[5]

The family of curves in Fig. 1 represents the dependence of longitudinal and transverse magnetostriction on the applied field H. All these curves were obtained for a single sample which was quenched from successively lower temperatures beginning at 1200°C. Each quench was preceded by heating to a temperature 100°C above the pre-quench temperature; this was followed by slow cooling at the rate of 50°C per hour to the required pre-quench temperature, which was maintained for long periods of time (from 4 hrs at 1200°C to 250 hrs at 100°C).

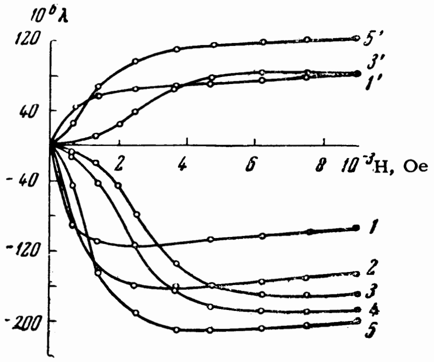

FIG. 1. Magnetostriction λ vs. the applied magnetic field H for cobalt ferrite quenched from different temperatures. Longitudinal magnetostriction $\lambda_{\parallel}$: quenched from 1 – 1200°, 2 – 500°, 3 – 200°, 4 – 300°, 5 – 400°C. Transverse magnetostriction $\lambda_{\perp}$: quenched from 1′ – 1200°, 3′ – 200°, 5′ – 400°C.

The curves in Fig. 1 show that both the maximum magnetostriction and the $\lambda(H)$ curves vary for different states of the sample. In samples quenched from high temperatures (1200–500°C) the absolute value of λ rises steeply in fields of $(1-2)\times 10^3$ Oe; this is followed by a linear decrease. Samples quenched from $T \leq 300°C$ exhibit a monotonic field dependence of λ, which remains constant up to 16×10^3 Oe after the saturation point is reached.

The field at which saturation is reached in a sample quenched from $\leq 300°C$ is three times higher than for the maximum of $|\lambda|$ in samples quenched from high temperatures. Figure 2 shows the dependence of saturation longitudinal magnetostriction λ_s^0 on T_q. The plotted values of λ_s^0 were obtained by extrapolating the straight segments of the $\lambda(H)$ curves to $H = 0$. This procedure was based on the hypothesis that the segments of the curves in Fig. 1 where $d\lambda_p/dH > 0$, resulted from positive volume magnetostriction due to the "paraprocess" (true magnetization).

Three distinct regions are observed on the curve of Fig. 2: 1) the region of high $T_q > 600°C$, characterized by constant λ_s^0; 2) the region from 600° to 200°C, where λ_s^0 depends nonmonotonically on T_q with its maximum at $T_q \approx 400°C$; 3) the region of relatively low $T_q \leq 200°C$, where λ_s^0 is constant. In a sample quenched from temperatures above 600°C, $|\lambda_s^0|$ is only one-half of its maximum value, and is smaller by a factor of one and one-half than in a sample cooled slowly to room temperature. The maximum of λ_s^0 for the different samples reaches a value of -250×10^{-6}.

It has thus been found that quenching from high temperatures fixes the state of a ferrite, which then at room temperature exhibits considerable volume magnetostriction that can be characterized[5] by the slope $d\lambda_p/dH$ of the straight segment of the $\lambda(H)$ curve. Figure 3 shows how the

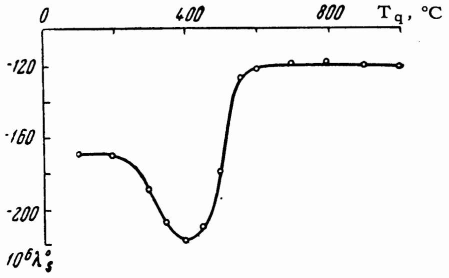

FIG. 2. Saturation longitudinal magnetostriction $\lambda_s°$ of cobalt ferrite vs. pre-quench temperature T_q.

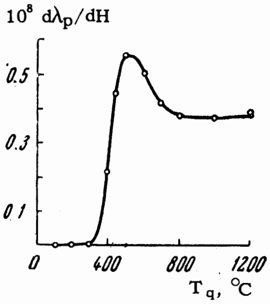

FIG. 3

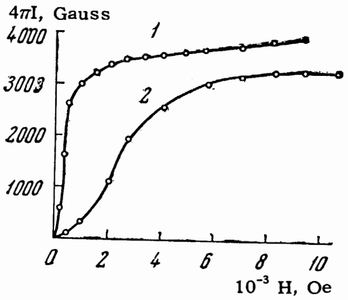

FIG. 4

FIG. 3. Slope $d\lambda_m/dH$ of straight segments of the $\lambda(H)$ curves vs. pre-quench temperature T_q for cobalt ferrite.

FIG. 4. Magnetization $4\pi I$ vs. magnetic field applied to pure cobalt ferrite: 1 – after quenching from 1000°C, and 2 – after quenching from 200°C.

values of $d\lambda_p/dH$ for the curves in Fig. 1 depend on the pre-quench temperature. This curve resembles the dependence of λ_s^0 on T_q. Specifically, the region where $d\lambda_p/dH$ increases markedly lies in the same temperature interval where $|\lambda_s^0|$ rises steeply.

The states of a sample quenched from different temperatures also differ with respect to other magnetic properties. Figure 4 shows magnetization as a function of the applied magnetic field for two states: 1) following prolonged annealing and quenching from 1000°C, and 2) following slow cooling and quenching from 200°C. Technical saturation is reached at different values of H. In the sample quenched from 1000°C magnetization continues to increase appreciably ($dI_s/dH = 0.005$ Gauss/Oe) after technical saturation is reached. For a sample that was cooled to relatively low temperatures ($T_q = 200$°C) we have $dI_s/dH = 0$.

4. The kinetics of the process of establishing high values of λ_s was investigated at different temperatures. Experiments were performed with samples of different porosities, quenched from 1200°C. The value of λ_s^0 corresponding to any given T_q is reached with increasing rapidity as the annealing temperature and porosity of a sample are increased. After relatively low-temperature annealing (300°—500°C) of samples quenched from high temperatures, $|\lambda_s^0|$ increases monotonically with time but with decreasing speed, until the limit for the given pre-quench temperature is reached. Annealing below 300°C after quenching from a high temperature has almost no effect on the value of λ_s^0, for the quenched sample, but only affects the dependence of λ on H. This anneal reduces the volume magnetostriction ($d\lambda_p/dH \rightarrow 0$), but the maximum of $|\lambda|$ is reached at a higher field strength.

5. Since in samples quenched from high temperatures and subsequently annealed during different periods of time at temperatures below 600°C the variation of λ_s^0 depends on porosity, it was naturally assumed that during the annealing process a ferrite interacts with the external atmosphere, i.e., it is oxidized in air.

We know [3] that magnetic annealing is sensitive to the amount of oxygen dissolved in the ferrite. A sample quenched from 1200°C was annealed for three hours at 300°C in a magnetic field. Oxidation during this magnetic anneal was avoided by placing the sample in a neutral (nitrogen) atmosphere. After the anneal λ_s^0 had the same value as for the initial state of the sample prior to the anneal. This indicates that quenching from a high temperature fixes a state that is close to the stoichiometric composition for which magnetic annealing has no effect.

When a ferrite is oxidized, after combining with excess oxygen it forms a substitutional solution with a cation deficit. The lattice constant a must then be decreased, because the cation diameter exceeds the linear size of the available sites. X rays were used to determine the relative changes of the lattice constant in a sample that was quenched successively from different temperatures. Figure 5 shows the dependence of $\Delta a/a$ on the pre-quench temperature. No change of a was observed after annealing in the range 1200—700°. A significant reduction of a occurs only after annealing in the range from 700° to 300°C, which includes the Curie point $\Theta = 520$°C.

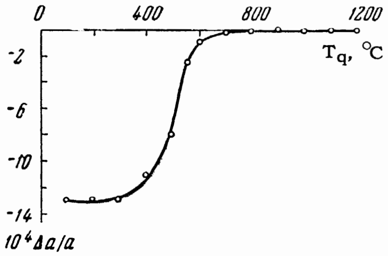

FIG. 5. Relative variation of the lattice constant, $\Delta a/a$ versus the pre-quench temperature T_q for cobalt ferrite.

Although the foregoing observation is consistent with the hypothesis that oxygen is dissolved in the ferrite lattice, this interpretation does not appear to be unique. A change of the lattice constant can have a different cause, such as the reordering of cations among tetrahedral and octahedral sites. If changes of λ_s and a result from oxidation and are not related to the reordering of the ions, then after prolonged annealing at T < 600°C while contact with oxygen is prevented, the structure and properties of samples should not be affected.

Indeed, it has been shown experimentally that in a sample annealed at 1200°C in a nitrogen atmosphere and subsequently annealed for 80 hours at 400°C in a 10^{-4}-mm vacuum within a sealed quartz ampoule, the measured values of λ_s and a were identical with their initial values. After annealing in a sealed evacuated ampoule at 400°C a small increase of $|\lambda_s|$ and the reduction of a occurred in a sample that had been annealed and quenched in air. This sample apparently already contained some amount of excess oxygen in an inactive form, so that in the initial state of the sample this oxygen had almost no effect on the structure and properties of the ferrite. Close values of the saturation longitudinal magnetostriction in the initial state were obtained after the first heat treatment in either nitrogen or air; these are $\lambda_s' = -100 \times 10^{-6}$ and $\lambda_s'' = -120 \times 10^{-6}$, respectively.

6. We reach the following conclusions from the foregoing investigation:

A. The saturation longitudinal and transverse magnetostrictions and their dependence on the applied magnetic field in pure cobalt ferrite vary considerably depending on the prior heat treatment. After prolonged annealing at high temperatures followed by quenching ($T_q \geq 600°C$), $|\lambda_q|$ has its minimum value for all variants of the heat treatment. The maximum absolute value $\lambda_s = -220 \times 10^{-6}$ follows slow cooling from high temperatures, prolonged baking at ≈ 400° C, and ultimate quenching. Slow cooling to relatively low temperatures ($T_q \leq 200°C$) yields $\lambda_s = -170 \times 10^{-6}$.

Quenching from 400°C and higher fixes the state of the cobalt ferrite that exhibits considerable volume magnetostriction due to the paraprocess in high fields. In this case the maximum value of $|\lambda|$ is reached in a field that is one-third of the field required for saturation magnetostriction in slowly cooled samples.

B. In the annealing range 300—700°C around the Curie point (520°C) the lattice constant of the ferrite decreases by about 0.1%; this appears to result from dissolution of oxygen in the lattice. Quenching from high temperatures fixes a state that is nearly stoichiometric with respect to the oxygen content and is insensitive to magnetic annealing.

In conclusion it is a pleasure to express my deep appreciation to Professor B. Ya. Pines for his assistance.

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[1] C. Guillaud, Revs. Modern Phys. 25, 64 (1953).

[2] R. Vautier, Compt. rend **235**, 356 (1952).

[3] B. Ya. Pines and N. M. Gumen, Kristallografiya **6**, 901 (1960), Soviet Phys. Crystallography 6, 727 (1962).

[4] L. Néel, Compt. rend **230**, 190 (1950).

[5] K. P. Belov, Uprugie, teplovye i élektricheskie yavleniya v ferromagnetikakh (Elastic, Thermal, and Electrical Phenomena in Ferromagnets), Gostekhizdat, 1957, pp. 78-88.

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