Observation of the spin-reorientation process by means of measurements of the magnetocaloric effect

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Measurements of the temperature and field dependence of the magnetocaloric effect (ΔT effect) are applied for observation of the process of spin reorientation, from the basal plane to the c axis, that occurs in a monocrystal of a hexagonal ferrite with the Co_xW structure ($x = 1.65$) upon rise of temperature. Because the contributions of the rotation and true magnetization processes to the total ΔT effect have different field dependences, measurements of the ΔT effect make possible a determination of the aperture angle of the cone formed by the spins during the reorientation process.

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Within definite compositions of hexagonal barium ferrites, the phenomenon of spin reorientation is observed. In order to study this phenomenon, we have applied a new method of investigation: measurements of the ΔT effect, which is an extremely sensitive energy characteristic of the state of the spin system and which enables one to trace the spin-reorientation process.

We chose a monocrystalline specimen of a hexagonal ferrite with the Co_xW structure, of composition $BaCo_{1.65}Fe^{2+}_{0.35}Fe^{3+}_{16}O_{27}$, grown from solution in the melt at the Institute of Crystallography of the USSR Academy of Sciences.1)

In hexaferrites of the system $BaCo_xFe_{18-x}O_{27}$, the orientation of the spins may vary, depending on the content of Co ions (for example, $x = 1.65$) and may change with change of temperature.[1] Thus if at room temperature the spins lie in the basal plane and the c axis is an axis of difficult magnetization, then with rise of temperature they leave the basal plane and form a cone of easy magnetization; with further rise of temperature, the spins orient themselves along the c axis, which at high temperatures becomes an axis of easy magnetization.2)

We carried out an investigation of the temperature and field dependence of the ΔT effect by a method described earlier.[2] In addition, by means of a rotating magnet and appropriate orientation of the specimen (Fig. 1) with respect to the c axis, we investigated the $\Delta T(\theta_c)$ dependence in the plane cOb, where θ_c is the angle between the direction of the field H and the c axis.

The ΔT effect that we measured contained contributions corresponding to the process of rotation of the vectors I_s and to the paraprocess.

It must be noted that the ΔT effect accompanying rotation of the vectors I_s will be larger in those magnetic materials in which the magnetic anisotropy energy has a larger value; such materials include, among ferromagnets, cobalt, and among ferrimagnets, hexagonal ferrites. In our specimen of a hexaferrite, besides the ΔT effect caused by rotation of the vectors I_s there was also a rather large ΔT effect from the paraprocess, even far from the Curie point, since in these ferrimagnets a strong paraprocess exists over a quite broad range of temperatures.[3]

Thus the integrated ΔT_{int} effect that we measured consisted of two components:

$$\Delta T_{int} = \Delta T_{rot} + \Delta T_{par}\,.$$

In ferromagnets, the magnetocaloric effect in the paraprocess region (ΔT_{par}) is positive, since orientation of the spins along the magnetic field is an energetically more favorable state and is therefore accompanied by liberation of heat.

It is known[4] that

$$\Delta T_{par} = -\frac{T}{C_{p,H}}\left(\frac{\partial I_s}{\partial T}\right)_H \Delta H, \tag{1}$$

where $C_{p,H}$ is the specific heat. Since $(\partial I_s/\partial T)_H < 0$ for the hexaferrite $Co_{1.65}W$,[1] we have from (1) $\Delta T_{par} > 0$. Thermodynamics enables us also to estimate the reversible change of temperature ΔT_{rot} that occurs on rotation of the vectors I_s.

Let θ_0 be the angle between the c axis and the direction of I_s, and θ_c the angle between the c axis and the direction of the external field H (Fig. 1). Then in strong magnetic fields, where the process of technical magnetization is complete and the vector I_s sets itself along H,

$$\Delta T_{rot} = \int_{\theta_0}^{\theta_K} dT,$$

it can be shown that

$$\Delta T_{rot} = \frac{T}{C_{p,H}}\left[\frac{\partial K_1}{\partial T}(\sin^2\theta_K - \sin^2\theta_0) + \frac{\partial K_2}{\partial T}(\sin^4\theta_K - \sin^4\theta_0) + \right.$$

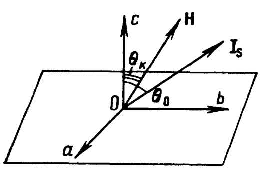

FIG. 1. Position of the vector I_s and H with respect to the c axis of the crystal. The axes a and b lie in the basal plane

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$$+\frac{\partial K_3}{\partial T}(\sin^6\theta_c-\sin^6\theta_0)\Big], \qquad (2)$$

where K_1, K_2, and K_3 are the magnetic anisotropy constants.

In the temperature range that we investigated ($T \sim 300$–700 K), the constant $K_3=0$ (K_3 vanishes at $T \sim 200$ K[1]), and formula (2) simplifies.

We remark that here we have not allowed for the effect of external and internal stresses on the magnetization but have introduced a correction for the demagnetizing field. On these assumptions, rotation of the vectors I_s will be opposed only by magnetic anisotropy forces.

As is seen from formula (2), ΔT_{rot} depends on the temperature behavior of the anisotropy constants, that is on the values of $\partial K_1/\partial T$ and $\partial K_2/\partial T$, and on the values of the differences of the squares and fourth powers of the sines of the angles at which the spins are directed with respect to the c axis, at the given temperature, and at which the external field is applied. The ΔT_{rot} effect is anisotropic, since there are terms in formula (2) that contain $\sin^2\theta$ and $\sin^4\theta$.

From analysis of formula (2) it is evident that if $\partial K_1/\partial T$ and $\partial K_2/\partial T$ have the same sign, the sign of the ΔT_{rot} effect depends on the angle at which **H** is applied. In the case when the spins have already left the basal plane and form a cone with aperture angle θ_0, the quantity $(\sin^2\theta_c - \sin^2\theta_0)$ will be negative when the field is applied at angles $\theta_c<\theta_0$ and positive when $\theta_c>\theta_0$. Correspondingly, the ΔT_{rot} effect is negative in the first case and positive in the second.

The presence of both negative and positive ΔT_{rot} effects is explained by the existence, in the temperature range 300–400 K, of two magnetic anisotropy constants, in consequence of which the processes of rotation of the vector $\mathbf{I}_s$ into the direction of **H** give different energy contributions when $\theta_c>\theta_0$ and when $\theta_c<\theta_0$.

From formula (2) it is also evident that the ΔT_{rot} effect is zero in those cases in which $\theta_c=\theta_0$; consequently, when $\theta_c=\theta_0$ the only contribution to the integrated ΔT_{int} effect will be ΔT_{par}, which far from the Curie temperature varies linearly with the field.

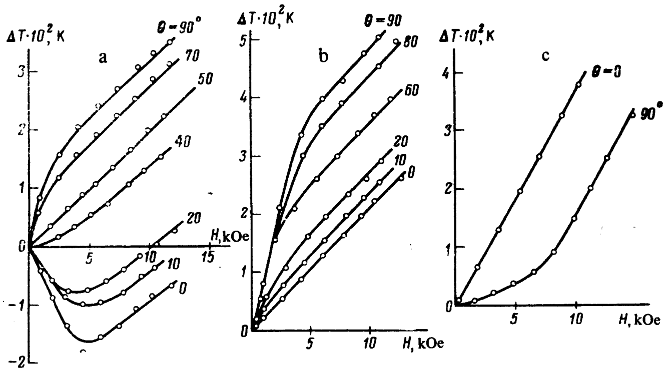

FIG. 2. Temperature dependence of $\Delta T_{int}(H)$ for various angles θ in the plane cOb, at temperatures: a, $T=329.5$ K; $\theta_0=50°$; b, $T=398$ K, $\theta_0=0$; c, $T=637$ K, $\theta_0=0$.

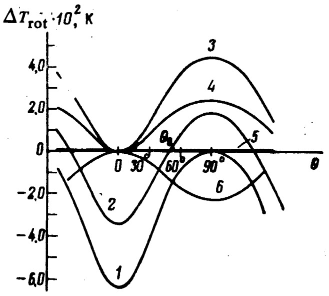

FIG. 3. $\Delta T_{rot}(\theta)$ curves calculated for various temperatures: 1, $T=296.7$ K; 2, $T=329.5$ K; 3, $T=398$ K; 4, $T=438$ K; 5, $T=545$ K; 6, $T=637$ K.

The difference in signs of the ΔT_{rot} effect will be reflected in the behavior of the $\Delta T_{int}(H)$ curves taken along different crystallographic directions. Experiment in fact substantiates the different behavior of $\Delta T_{int}(H)$ curves taken at the same temperature along different crystallographic directions (Fig. 2a). From Fig. 2a it is seen that for directions of **H** that make angles 0, 10, 20, and 40° with the c axis, the effects of rotation make a negative contribution to the ΔT_{int} effect, but for directions 70 and 90° a positive; only for a direction of **H** that coincides with the direction of the spins at the given temperature does the contribution of rotation processes to the ΔT_{int} effect vanish ($\theta_0=50°$ for $T=329.5$ K): $\Delta T_{int}(H)_{\theta_c=\theta_0}$ is a straight line passing through the origin.

Thus measurements of the ΔT effect enable us to determine the aperture angles of the cone in the spin-reorientation process.

We carried out a theoretical analysis of formula (2) for the spin-reorientation process ($0\leq\theta_0\leq 90°$), neglecting anisotropy in the basal plane, with known values of $K_1(T)$ and $K_2(T)$ taken from the paper of Perekalina *et al.*[1] and with angles θ_0 determined by us. This series of calculated curves is shown in Fig. 3 for various temperatures.[3)] Curve 1 corresponds to 296.7 K. At this temperature, the spins lie in the basal plane, and the ΔT_{rot} effect is negative for all field directions (in the plane cOb); the minimum corresponds to the c axis ($\theta=0$), the direction of difficult magnetization, and the maximum ($\theta=90°$) to the direction of easy magnetization (the zero value of ΔT_{rot} corresponds to $\theta=90°$, where the $\Delta T(\theta)$ curve is tangent to the axis of abscissas). With rise of temperature the spins leave the basal plane, forming a cone with aperture angle θ_0. Curve 2 is drawn for $T=329.5$ K, at which $\theta_0=50°$ (see the section $O\theta_0$ in Fig. 3 and the curve $\Delta T_{int}(H)$ for $\theta=50°$ in Fig. 2a). At this temperature $\theta_0=50°$ is the direction of easy magnetization, while the c axis and the basal plane ($\theta=0°$ and $\theta=90°$) are directions of difficult magnetization. ($\theta=0°$ is harder than $\theta=90°$, since $|\Delta T_{rot\,0°}|>|\Delta T_{rot\,90°}|$.) With further rise of temperature the $\Delta T_{rot}(\theta)$ curve rises higher, the cone aperture meanwhile gradually decreases, and at $T=398$ K (curve 3 of Fig. 3) the spins are oriented along the c axis, which becomes an axis of easy magnetization ($\Delta T_{rot}=0$ at $\theta_0=0$); this is also clearly evident from Fig. 2b. The largest value of ΔT_{rot} occurs at $\theta=90°$ (the basal plane),

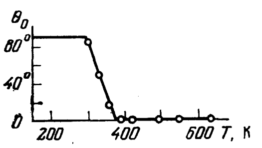

FIG. 4. Temperature dependence of cone aperture angle θ_0 during the process of reorientation of spins to the c axis, as determined from measurements of the ΔT-effect for a Co_xW monocrystal ($x = 1.65$).

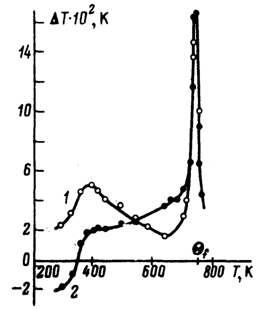

FIG. 6. The functions (1) $\Delta T_{b.pl.}(T)$ and (2) $\Delta T_c(T)$ at $H = 10$ kOe.

which is the direction of most difficult magnetization, although the contribution of rotation processes is positive. On subsequent rise of temperature the c axis becomes an axis of easy magnetization and the basal plane a direction of difficult magnetization. The contribution of ΔT_{rot} continues to be positive but gradually decreases (in the temperature range $T > \sim 430$ K, the constant $K_2 = 0$, and the value of $\partial K_1/\partial T > 0$ also gradually decreases), up to temperature ~ 545 K, at which the contribution of rotation processes vanishes. (At $T \sim 545$ K the value of $\partial K_1/\partial T$ vanishes, since the $K_1(T)$ curve goes through a maximum.[1]) In Fig. 3 these temperatures correspond to curves 4 and 5 (5 is a straight line coincident with the abscissa axis, $\Delta T_{rot} = 0$).

The $\Delta T_{int}(H)$ curves, which are similar to the curves in Fig. 2b, at these temperatures gradually approach each other, merging with the straight line $\theta_0 = 0$ for $T \sim 545$ K. At this temperature the crystal becomes isotropic. At $T > 545$ K the anisotropy constant K_1 gradually decreases, and $\partial K_1/\partial T < 0$. The contribution of rotation processes becomes negative (see curve 6 in Fig. 3); the c axis remains a direction of easy magnetization and the basal plane a direction of difficult magnetization, but for $T > 545$ K it corresponds to a minimum and not a maximum on the $\Delta T_{rot}(\theta)$ curves; this is related to the negative contribution of rotation processes.

The $\Delta T_{int}(H)$ curve for $\theta = 90°$ in Fig. 2c is now located not above but below the straight line for $\theta = 0°$. Figure 4 shows the angles, as we have determined them, at which the spins are oriented during the reorientation process.

The spin-reorientation process that we have described can also be traced in Figs. 5 and 6. Figure 5 shows the curves of $\Delta T_{int}(\theta) = \Delta T_{rot} + \Delta T_{par}$ taken at various temperatures; their behavior is clear without additional explanation, with allowance for the fact that the intensity of the paraprocess increases with rise of temperature, so that the $\Delta T_{int}(\theta)$ curves are located higher and higher as the temperature rises. We note also that the $\Delta T_{int}(\theta)$ curve taken at $T \sim 545$ K actually has no distinctive features, since the contribution of ΔT_{par} is isotropic and positive. Figure 6 shows the function $\Delta T(T)$ measured along the c axis and along the basal plane. According to[5] the spin-reorientation process is accompanied by two phase transitions of the second kind. On the $\Delta T_c(T)$ and $\Delta T_{b.pl.}(T)$ curves (Fig. 6), anomalies are noticeable in the range $T \sim 390$–400 K; this corresponds to the second phase transition of the second kind, completion of the reorientation of the spins to the c axis. The c axis, as we have seen above, has already become an axis of easy magnetization at $T \sim 398$ K, but the $\Delta T_{b.pl.}$ curve remains above the ΔT_c curve because of the positive contribution of the rotation processes to the total ΔT effect. At $T \sim 545$ K the crystal becomes isotropic, and for $T > 545$ K the contribution of the effects of rotation becomes negative and the $\Delta T_{b.pl.}$ curve lies below the ΔT_c curve (Fig. 6). Near the Curie temperature Θ_f, domain structure disappears, and the curves taken in different directions come together; the role of the paraprocess grows, and on the $\Delta T(T)$ curve there is at $T = \Theta_f$ a sharp maximum of the ΔT effect, whose value is the same for the directions of easy and of difficult magnetization.

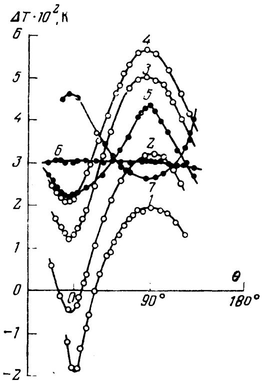

FIG. 5. The function $\Delta T_{int}(\theta)$ measured at $H = 10$ kOe, for temperatures: 1, $T = 291.8$ K; 2, $T = 343.2$ K; 3, $T = 368$ K; 4, $T = 387$ K; 5, $T = 452$ K; 6, $T = 545$ K; 7, $T = 641.5$ K.

In conclusion we note that, as has been shown by investigations conducted earlier by Ivanovskiǐ for Co[6] and by our investigations for hexaferrite, although rotation of the vectors I_s in the direction of the applied external field leads to an increase of the magnetic anisotropy energy, the model representations alone are still insufficient for the determination of the sign of the thermal effect from rotation processes; a more detailed analysis is needed both of the temperature behavior of the anisotropy constants and of the correlation in the positions of the external field and of the spins at a given temperature.

Thus we have established that measurements of the magnetocaloric effect, which is a very sensitive energy characteristic of magnetization processes, enable us not only to observe the spin-reorientation process, but also to determine the aperture angle of the cone—the spin position—during the reorientation process.

In conclusion, the authors thank R. Z. Levitin, Doctor of Physico-Mathematical Sciences, for a number of useful discussions of the results of the research.

[1)] The authors thank T. M. Perekalina for providing the specimen.

[2)] Noticeable anisotropy in the basal plane occurs only at temperatures below 200 Å.[1]

[3)] To eliminate the crude errors in a determination of $\partial K_1/\partial T$ and $\partial K_2/\partial T$ by a graphical method, we approximated the $K_1(T)$ and $K_2(T)$ curves analytically.

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Low-temperature photoluminescence of gallium arsenide

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The emission spectra of gallium arsenide with different contents of impurities were investigated in a wide range of excitation levels. It is shown that the dominant recombination channel of the free excitons is captured by shallow donors and acceptors followed by very rapid annihilation of the exciton-impurity complexes. When the excitation density increases to $n_{cr} \sim 10^{15}$ cm^{-3}, the free-carrier gas condenses into electron-hole drops with equilibrium density $n_0 \sim 10^{16}$ cm^{-3}.

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1. INTRODUCTION

A rather large number of various collective effects in semiconductors are presently discussed in the literature. One of the most interesting manifestations of collective interactions should be taken to be the condensation of excitons into electron-hole drops (EHD). This phenomenon has been investigated in sufficient detail in the indirect semiconductors Ge and Si, and most experiments have been explained not only qualitatively but also quantitatively.

In semiconductors with direct allowed transitions, the possibility of condensation of excitons or of free carriers is denied by most workers, because of the short lifetime of the gas phase ($\tau \sim 10^{-9}$ sec). To explain the observed emission spectra at high excitation levels in straight-band semiconductors it is therefore customary to resort to the so-called collective radiative processes, such as inelastic exciton–exciton collisions (the P band),[1] inelastic collisions of biexcitons,[2] etc. In addition, the contribution of the radiation of the electron-hole plasma,[3] i.e., of interband recombination with allowance for the change of the width of the forbidden band as a result of the collective interactions, is also considered.

The short lifetimes of the free excitons in semiconductors with direct allowed transitions notwithstanding, one can apparently not exclude the possibility of experimental observation of EHD. It can be shown[4] that EHD with equilibrium density n_0 and radius R should be produced at $n_{av} \gtrsim n_0 R/3\tau_0 v_{av}$, where n_{av} is the average density of the condensing gas, v_{av} is the average thermal velocity, and τ_0 is the lifetime. Estimates show that in gallium arsenide (GaAs) at $n_{av} \sim 10^{15}$ cm^{-3} there can exist EHD with radius $R \sim 10^{-4}$ cm and equilibrium density $n_0 \sim 10^{16}$ cm^{-3} [5] at $\tau_0 \sim 10^{-9}$ sec. It should be noted here that $n_{av} \sim 10^{15}$ cm^{-3} seems to exclude completely a contribution of free excitons to the condensed phase, since there can be no free excitons in GaAs at these densities. What should be condensed in this case are the free carriers, as is indeed confirmed by experiment.[6,7]

2. FEATURES OF RADIATIVE RECOMBINATION IN GaAs

One of the most important characteristics of optical transitions in solids is the oscillator strength f_i for processes in which light is absorbed, or the radiative lifetime τ_i in the case of emission. If we disregard the dispersion of the dielectric constant, then $\tau_i = 3m_0c^3/2e^2n\omega_i^2 f_i$, where m_0 is the mass of the free electron, n is the refractive index, and ω_i is the frequency of the light.

Using the known expression for the oscillator strength[8] in the case of direct allowed transitions, we can estimate the radiative lifetime of the free excitons $\tau_{ex} \sim 5 \cdot 10^{-5}$ sec in GaAs.

However, if the crystal contains impurities (shallow donors and acceptors), then the free excitons can become bound to form exciton-impurity complexes.[9]

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