Surface reorientation transitions

M. I. Kaganov

Institute of Physical Problems, Academy of Sciences, USSR
(Submitted 25 April 1980)
Zh. Eksp. Teor. Fiz. **79**, 1544–1553 (October 1980)

The effect of surface magnetic-anisotropy energy on spin-flip transitions, caused by change of sign of the first anisotropy constant k_1, is investigated. It is shown that, first, transitions within the volume should be accompanied by surface transitions (which under certain conditions are of second order); and second, the hysteresis loops should change their shape (become narrower). This change is independent of the specimen dimensions. The effect of surface fluctuations is considered, and a criterion is formulated for applicability of Landau's theory (without allowance for fluctuations) to surface reorientation transitions of the second order.

PACS numbers: 75.30.Kz, 75.30.Gw

1. INTRODUCTION

Spin-flip transitions in magnetic materials, which have been studied intensively in recent years,[1] can be described by introduction of an effective anisotropy constant k_1 that changes sign with change of temperature [$k_1=\beta(T-T_0)/T_0=\beta\tau$; for definiteness, $\beta>0$]. The treatment as a rule can be reduced to investigation of the anisotropy energy

$$M^{-1}F_V(\vartheta)=f_V(\vartheta)=-k_1\sin^2\vartheta-k_2\sin^4\vartheta, \tag{1}$$

where M is the magnetic moment of unit volume (in the simplest case of a uniaxial ferromagnet, $M=\mu/a^3$, where μ is the Bohr magneton and a is the interatomic distance), and where k_2 is the second anisotropy constant ($|k_2|\ll|k_1|$ far from $T=T_0$). The nature of the transition within the volume is determined by the sign of k_2: when $k_2>0$, the transition from the state with $\theta=0$ to the state when $\theta=\pi/2$ occurs as a transition of first order (Figs. 1 and 2); when $k_2<0$, as two transitions of second order located close together (Figs. 3 and 4). As for any transition of second order, in the neighborhood of reorientational phase transitions [$k_1\approx k_{c1}=0$ and $k_1=k_{c2}=2|k_2|$ (see Figs. 2 and 4)] the role of fluctuations is anomalously large. But because of the fact that the inhomogeneous part of the free energy is determined by the comparatively large exchange forces, and the reorientation by the temperature dependence of the small (relativistic) anisotropy constants, the condition for applicability of the Landau theory (the Levanyuk-Ginzburg criterion; see Ref. 2, § 146) is violated only in the immediate vicinity of the transition point. On adding to $f_V(\theta)$ the energy of nonuniform exchange $C(d\theta/dx)^2$, where $C=a^2\Theta/\mu M$ (Θ is a quantity of the order of magnitude of the Curie temperature), one can easily show that the Landau theory is valid when

$$|k_1-k_c|\gg k_2(T_0/\Theta)^2\mu M/\Theta,$$

that is, over practically the whole range of k_1 values of interest to us ($|k_1|\lesssim|k_2|$; see Figs. 2 and 4). The applicability of the expansion (1) to the case of a phase transition of first order is justified by the fact that this is an expansion not in an order parameter but (essentially) in the ratio v_a/c (v_a is the velocity of the atomic electrons, c the velocity of light; see Ref. 3, §37).

In a surface layer, the anisotropy constants must differ substantially from their bulk values. Here, of course, there may be a change not only of the value of the constant but also of the direction of the axes of easy and hard magnetization. Both these facts are taken into account by introduction of a surface anisotropy energy f_S, which without loss of generality may be represented in the form[1)]

$$f_s=k_s\sin^2(\vartheta_s-\varphi), \tag{2}$$

where k_S is the surface-anisotropy constant, θ_S is the value of the angle θ at the surface of the specimen ($x=0$), and the angle φ, for $k_S>0$, gives the direction of the axis of easiest magnetization on the surface (k_S, in contrast to K_1 and k_2, has the dimension of length; k_1 and k_2 are dimensionless quantities).

There is no reason to expect that k_S will vanish in the same temperature range where k_1 changes sign. This permits us to restrict ourselves to the first term of the expansion, written in (2).

Our problem consists in the elucidation of the effect of the surface energy (2) on the reorientational transitions; for this purpose, it is necessary to investigate the functional

$$M^{-1}F_s\{\vartheta(x)\}=\int_0^\infty\{f_V(\vartheta)-f_V(\vartheta_\infty)+C(d\vartheta/dx)^2\}dx+k_s\sin^2(\vartheta_s-\varphi), \tag{3}$$

where θ_∞ is the equilibrium value (stable or metastable) of the angle θ in the depth of the specimen (at $x\to\infty$).

The function $\theta(x)$ that minimizes the functional (3) satisfies the equation

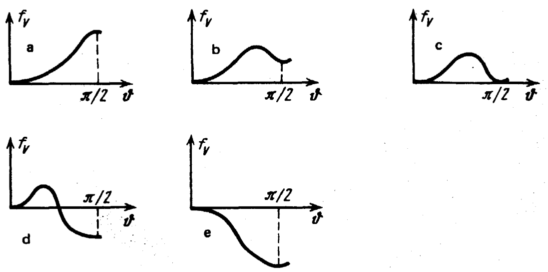

FIG. 1. Variation of anisotropy energy with direction of magnetic moment within the volume when $k_2>1$: a, $k_1<-2k_2$; b, $-2k_2<k_1<-k_2$; c, $k_1=-k_2$; d, $-k_2<k_1<0$; e, $k_1>0$.

 0038-5646/80/100779-05$02.40

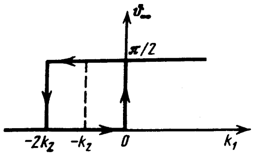

FIG. 2. Hysteresis loop when $k_2 > 0$.

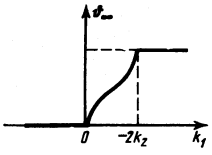

FIG. 4. Variation of direction of magnetic moment within the volume with k_1, when $k_2 < 0$.

$$\frac{\partial f_V(\vartheta)}{\partial\vartheta}-2C\frac{d^2\vartheta}{dx^2}=0 \qquad (4)$$

and the boundary conditions

$$\left.\frac{d\vartheta}{dx}\right|_{x=0}=\frac{k_S}{2C}\sin 2(\vartheta_S-\varphi), \qquad (5)$$

$$\left.\frac{d\vartheta}{dx}\right|_{x\to\infty}=0, \qquad \vartheta|_{x\to\infty}=\vartheta_\infty. \qquad (5')$$

According to (4) and (5′)

$$C(d\vartheta/dx)^2=f_V(\vartheta)-f_V(\vartheta_\infty). \qquad (6)$$

The sign of $d\theta/dx$ coincides with the sign of $\theta_\infty-\theta_S$;

$$\frac{d\vartheta}{dx}=\frac{\operatorname{sign}(\vartheta_\infty-\vartheta_S)}{C^{1/2}}[f_V(\vartheta)-f_V(\vartheta_\infty)]^{1/2}. \qquad (7)$$

The last equation[2] enables us to give the boundary condition (5) the following form:

$$\operatorname{sign}(\vartheta_\infty-\vartheta_S)[f_V(\vartheta_S)-f_V(\vartheta_\infty)]^{1/2}=\frac{k_S}{2C^{1/2}}\sin 2(\vartheta_S-\varphi). \qquad (8)$$

Substitution of the value of $d\theta/dx$ in (3) enables us to transform the functional (3) to a function of θ_S:

$$\frac{F(\vartheta_S)}{2M^2C^{1/2}}=\operatorname{sign}(\vartheta_S-\vartheta_\infty)\int_{\vartheta_\infty}^{\vartheta_S}d\vartheta[f_V(\vartheta)-f_V(\vartheta_\infty)]^{1/2}+\frac{k_S}{2C^{1/2}}\sin^2(\vartheta_S-\varphi), \qquad (9)$$

then the boundary condition (8) is the condition for an extremum of the function $F(\theta_S)$. To the stable solution, of course, corresponds that root of Eq. (8) for which $F(\theta_S)$ has a minimum; that is,

$$\frac{F''(\vartheta_S)}{2M^2C^{1/2}}=\frac{\operatorname{sign}(\vartheta_S-\vartheta_\infty)f_V'(\vartheta_S)}{2[f_V(\vartheta_S)-f_V(\vartheta_\infty)]^{1/2}}+\frac{k_S}{C^{1/2}}\cos 2(\vartheta_S-\varphi)>0. \qquad (10)$$

2. SURFACE TRANSITIONS DURING A VOLUME TRANSITION OF FIRST ORDER ($k_2>0$)

We begin with a negative first anisotropy constant ($k_1 < 0$). When $k_1 < -k_2$, the state with $\theta_\infty=0$ is stable within the volume; when $-k_2 < k_1 < 0$, this state is metastable. We shall seek a minimum of $F(\theta_S)$ when $\theta_\infty=0$. If the axes of easy magnetization within the volume and on the surface coincide ($\varphi=0$), then $\theta(x)\equiv 0$.

We first consider the case in which the surface axis is not perpendicular to the volume axis ($\varphi\neq\pi/2$). It is obvious that the angle θ_S must lie between 0 and φ. On substituting the value of $f_V(\theta)$ and taking into account that $f_V(\theta_\infty)=0$, whereas $d\theta/dx<0$, we have

$$\sin\vartheta_S\left(\frac{|k_1|}{k_2}-\sin^2\vartheta_S\right)^{1/2}=\frac{1}{2}\sigma\sin 2(\varphi-\vartheta_S), \qquad \sigma=\frac{k_S}{(Ck_2)^{1/2}}, \qquad (11)$$

$$\frac{\cos\vartheta_S(|k_1|/k_2-2\sin^2\vartheta_S)}{(|k_1|/k_2-\sin^2\vartheta_S)^{1/2}}+\sigma\cos 2(\vartheta_S-\varphi)>0. \qquad (11')$$

Figure 5 shows a graphic solution of Eq. (11). For sufficiently large values of $|k_1|/k_2$, the equation has only one root. Since $F'(\theta_S=0)<0$, it corresponds also to a minimum. For smaller values of $|k_1|/k_2$, Eq. (11) has two roots: the smaller corresponds to a minimum, the larger to a maximum. There is a value of $|k_1|$ (we denote it by $|k_{1c}|$) such that when $|k_1|<|k_{1c}|$, there are no roots. The values of $|k_{1c}|$ and θ_c [θ_c is the multiple root of Eq. (11)] are determined by solution of the system of equations

$$\sin\vartheta_c(|k_{1c}|/k_2-\sin^2\vartheta_c)^{1/2}={}^1/_2\sigma\sin 2(\varphi-\vartheta_c),$$
$$\frac{\cos\vartheta_c(2\sin^2\vartheta_c-|k_{1c}|/k_2)}{(|k_{1c}|/k_2-\sin^2\vartheta_c)^{1/2}}=\sigma\cos 2(\vartheta_c-\varphi). \qquad (12)$$

The parameter σ that occurs in Eqs. (11) and (12) is a measure of the surface energy. Since $k_S=\bar{k}_S a$, where $\bar{k}_S$ is a dimensionless quantity of the same nature as k_1 and k_2 (as a rule, $\bar{k}_S\gg|k_1|$), $\sigma=k_S(\mu M/k_2\Theta)^{1/2}$ may be either larger or smaller than unity. We shall consider the two limiting cases ($\sigma\gg 1, \sigma\ll 1$).

We begin with the calculation of $|k_{1c}|/k_2$ and θ_c:

$$\vartheta_c\approx({}^1/_2\sigma\sin 2\varphi)^{1/3}, \quad |k_{1c}|/k_2\approx 2({}^1/_2\sigma\sin 2\varphi)^{2/3}, \quad \sigma\ll 1,$$
$$\vartheta_c\approx\varphi-\sin^3\varphi\cos\varphi/\sigma^2, \quad |k_{1c}|/k_2\approx\sin^2\varphi(1+\sin^2 2\varphi/4\sigma^2), \quad \sigma\gg 1. \qquad (13)$$

If $|k_1|\gg|k_{1c}|$, then

$$\vartheta_S\approx\sigma\sin 2\varphi/2(|k_1|/k_2)^{1/2}\ll 1. \qquad (14)$$

But when $\sigma\gg 1$, this formula is valid only at very large values of $|k_1|/k_2$ ($|k_1|/k_2\gg\frac{1}{4}\sigma^2\sin^2 2\varphi$). In the opposite limiting case,

$$\vartheta_S\approx\varphi-\frac{\sin\varphi}{\sigma}\left(\frac{|k_1|}{k_2}\right)^{1/2}. \qquad (15)$$

If $|k_1|\approx|k_{1c}|$, then $\theta_S\approx\theta_c-A(k_{1c}-k_1)^{1/2}$; the coefficient A is determined by the value of $F'''(\theta_c)$. The last formulas show that the surface energy shifts the lability point somewhat: the state with $\theta_\infty=0$ becomes absolutely unstable not when $k_1=0$, but when

$$k_1=k_{1c}\approx\begin{cases}-(k_Sk_2\sin 2\varphi)^{2/3}(2/C)^{1/3}, & k_S/(k_2C)^{1/2}\ll 1,\\ -k_2\sin^2\varphi, & k_S/(k_2C)^{1/2}\gg 1.\end{cases} \qquad (16)$$

We now consider the case in which the surface and volume axes of anisotropy are perpendicular to each

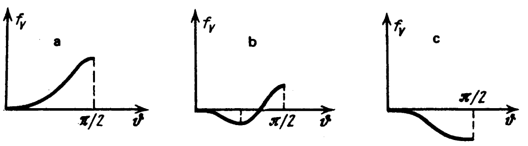

FIG. 3. Variation of anisotropy energy with direction of magnetic moment within the volume when $k_2<0$: a, $k_1<0$; b, $0<k_1<2|k_2|$; c, $k_1>2|k_2|$.

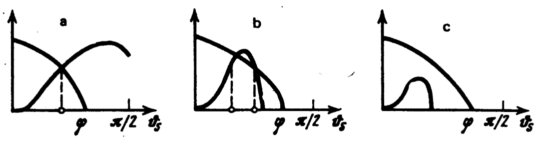

FIG. 5. Graphic solution of Eq. (11) ($k_1<0$, $k_2>0$): a, $|k_1|$ k_2; b, $|k_c|<|k_1|<k_2$; c, $|k_1|<|k_c|$.

other ($\varphi=\pi/2$). In this case, Eq. (11) has two solutions:

$$\sin\vartheta_s=0,\quad \sin\vartheta_s=[(|k_1|/k_2-\sigma^2)/(1-\sigma^2)]^{1/2}.$$

The second root exists if

$$\sigma^2<|k_1|/k_2<1$$

or

$$1<|k_1|/k_2<\sigma^2.$$

The values of the second derivative F'' at the extremum point are proportional to $(|k_1|/k_2)^{1/2}-\sigma$ for the first root and to $(\sigma-1)\sin^2\theta_S$ for the second.

Thus if $\sigma<1$, there is only one solution $\theta_S=0$; this means that when $|k_1|/k_2>\sigma^2$, the direction of the magnetic moment is uniform over the whole body $[\theta(x)\equiv 0]$, and the lability point is

$$k_1=k_{1c}=-k_2\sigma^2,\quad \varphi=\pi/2,\quad \sigma<1. \tag{17}$$

If $\sigma>1$, then at $|k_1|/k_2=\sigma^2$ a new solution appears, corresponding to a minimum,

$$\sin\vartheta_s=\left(\frac{\sigma^2-|k_1|/k_2}{\sigma^2-1}\right)^{1/2}, \tag{18}$$

that is, when $|k_1|/k_2=\sigma^2>1$ there should be observed a surface phase transition of the second order. When $|k_1|=k_2$, the angle θ_S reaches the value $\pi/2$, and consequently $k_1=-k_2$ in this case: a lability point of the state with $\theta_\infty=0$.

We turn now to consideration of states with $\theta_\infty=\pi/2$. Without allowance for boundaries, they are stable when $k_1>-k_2$ and metastable when $-2k_2<k_1<-k_2$. Now, $\varphi<\theta_S<\pi/2$ (φ of course is not equal to $\pi/2$; when $\varphi=\pi/2$, the boundary makes no change in the state diagram). It is easily verified that, with the notation

$$\vartheta_s=\pi/2-\chi,\quad 2k_2+k_1=k_1^*,\quad \varphi^*=\pi/2-\varphi, \tag{19}$$

Eq. (8) can be given the form, coinciding with (11),

$$\sin\chi(k_1^*/k_2-\sin^2\chi)^{1/2}={}^1/_2\sigma\sin 2(\varphi^*-\pi/2). \tag{19'}$$

This enables us to use the results obtained above.

Figure 6 shows the function $\theta_S=\theta_S(k_1)$, a surface hysteresis loop for $\varphi\neq\pi/2$. We note some features of this loop: $d\theta_S/dk_1$ becomes infinite at the lability points: although the phase-equilibrium line ($k_1=-k_2$) is practically unshifted [the shift is an effect of order $(\Theta/\mu M)^{1/2}(a/L)$, where L is a dimension of the body], the change of width of the hysteresis loop is an observable effect, since it is independent of the specimen dimensions.[3)]

Figure 7 shows the function $\theta_S(k_1)$ for $\varphi=\pi/2$. The form of the hysteresis loop depends on the value of the surface energy: when $\sigma<1$, the surface hysteresis loop has the form of a rectangle (Fig. 7a); when $\sigma>1$, there should occur a phase transition of second order at $k_1=-\sigma^2k_2$; in the immediate vicinity of the lability point

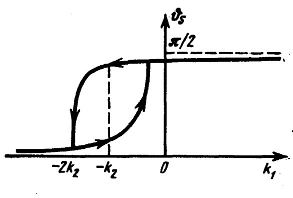

FIG. 6. Surface hysteresis loop for $\varphi\neq\pi/2$; (variation of θ_S with k_1 when $k_2>0$).

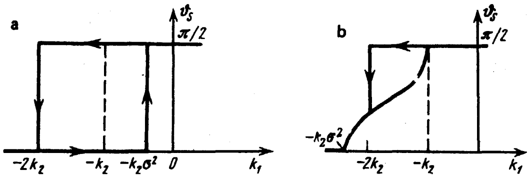

FIG. 7. Surface hysteresis loop for $\varphi=\pi/2$ (variation of θ_S with k_1 when $k_2>0$): a, $\sigma<1$; b, $\sigma>1$.

$k_1=-k_2$, the state with $\theta_\infty=0$ is already metastable (the phase-equilibrium line with allowance for surface energy moves slightly to the left). It is interesting to note that when $k_1>-k_2$, there is no metastable state with $\theta_\infty=0$.

3. THE θ_s (k_1) RELATION DURING A VOLUME TRANSITION OF SECOND ORDER ($k_2<0$)

The anisotropy energy

$$f_V(\vartheta)=-k_1\sin^2\vartheta+|k_2|\sin^4\vartheta \tag{20}$$

always has one minimum when k_2 is negative (see Fig. 3). When $k_1<0$, the angle θ_∞ is zero; when $0<k_1<2|k_2|$, we have $\sin\theta_\infty=(k_1/2|k_2|)^{1/2}$; and when $k_1\geqslant 2|k_2|$, the angle θ_∞ is $\pi/2$. The change of θ_∞ with k_1 (Fig. 4) leads to the result that when $0<k_1/2|k_2|<\sin^2\varphi$, there occurs a state that monotonically decreases from the boundary ($d\theta/dx<0$); and when $k_1/2|k_2|>\sin^2\varphi$, one that monotonically increases ($d\theta/dx>0$). When $k_1/2|k_2|=\sin^2\varphi$, the uniform state is stable.

When $\theta_\infty=0$ ($k_1<0$), the equations analogous to (11) have the form

$$\sin\vartheta_S\left(\left|\frac{k_1}{k_2}\right|+\sin^2\vartheta_S\right)^{1/2}=\frac{1}{2}\sigma\sin 2(\varphi-\vartheta_S),\quad \sigma=\frac{k_S}{(|k_2|C)^{1/2}},$$
$$\frac{\cos\vartheta_S(|k_1/k_2|+2\sin^2\vartheta_S)}{(|k_1/k_2|+\sin^2\vartheta_S)^{1/2}}+\sigma\cos 2(\vartheta_S-\varphi)>0. \tag{21}$$

It is evident that a solution always exists and that it always corresponds to a minimum:

$$\vartheta_S=\begin{cases}\sigma\sin 2\varphi/2(|k_1/k_2|)^{1/2}, & \sigma\ll|k_1/k_2|,\\ \varphi-\sigma^{-1}\sin\varphi(|k_1/k_2|+\sin^2\varphi)^{1/2}, & \sigma\gg|k_1/k_2|.\end{cases}$$

When $\sin\theta_\infty=(k_1/2|k_2|)^{1/2}$, the equation for determination of θ_S looks especially simple:

$$\sin^2\vartheta_S-\sin^2\vartheta_\infty={}^1/_2\sigma\sin 2(\varphi-\vartheta_S),\quad k_1>0. \tag{22}$$

Hence for small $\sigma(\sigma\ll\sin\theta_\infty)$

$$\sin\vartheta_s\approx\sin\vartheta_\infty+\sigma\sin 2(\varphi-\vartheta_\infty)/4\sin\vartheta_\infty, \tag{23}$$

and for large $\sigma(\sigma\gg\sin\theta_\infty)$

$$\vartheta_S\approx\varphi+\sigma^{-1}(\sin^2\varphi-\sin^2\vartheta_\infty). \tag{24}$$

When $\theta_\infty=\pi/2$ ($k_1\geqslant 2|k_2|$), a substitution analogous to (19),

$$k_1-2|k_2|\to|k_1|,\quad \pi/2-\vartheta_S\to\vartheta_S,\quad \pi/2-\varphi\to\varphi, \tag{F}$$

reduces this case to the case $\theta_\infty=0$. Thus θ_S, as well as θ_∞, is a single-valued function of k_1, evidently having no singularities [at $k_1=0$, the angle $\theta_S=\theta_S(k_1)$ and its first derivative are continuous; see Fig. 8a].

We consider the case $\varphi=\pi/2$ separately. Proceeding as before, we find

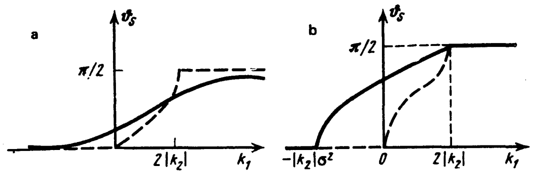

FIG. 8. The function $\theta_S = \theta_S(k_1)$ when $k_2 < 0$: a, $\varphi \neq \pi/2$; b, $\varphi = \pi/2$. Dotted curve: the functions $\theta_\infty = \theta_\infty(k_1)$.

$$\sin^2\vartheta_s = \begin{cases} 0, & k_1 \leqslant -\sigma^2|k_2|, \\ (2a+\sigma^2)/(1+\sigma^2), & -\sigma^2|k_2| \leqslant k_1 < 0, \quad a = k_1/2|k_2|, \\ \dfrac{2a+\sigma^2+\sigma[\sigma^2+4a(1-a)]^{1/2}}{2(1+\sigma^2)}, & 0 < k_1 < 2|k_2|, \\ 1, & k_1 > 2|k_2|. \end{cases}$$

Thus the transition from the state $\theta \equiv 0$ to the state $\theta \equiv \pi/2$ is preceded by three phase transitions: one surface phase transition of second order at $k_1 = -|k_2|\sigma^2$ and two volume transitions (at $k_1 = 0$ and at $k_1 = 2|k_2|$). At the point $k_1 = 0$, θ_S and $d\theta_S/d\tau$ are continuous; but at the point $k_1 = 2|k_2|$, $d\theta_S/dk_1$ has a finite discontinuity (Fig. 8b)

$$\left.\frac{d\vartheta_s}{dk_1}\right|_{k_1=2|k_2|-0} = (2^{1/2}\sigma|k_2|)^{-1}. \tag{26}$$

4. DEPTH OF PENETRATION

An important characteristic of a surface state is the depth of penetration, which, because of the complicated spatial variation $\theta(x)$, can be defined in various ways. In the immediate vicinity of the boundary (for $x \to 0$), the spatial variation $\theta(x)$ is conveniently characterized by the quantity

$$\delta_s = \vartheta_s \Big/ \left(\frac{d\vartheta_s}{dx}\right)_{x=0},$$

which according to (7) and (8) can be exhibited in the following form:

$$\delta_s = \frac{C}{k_s}\frac{2\vartheta_s}{\sin 2|\vartheta_s - \varphi|} = \frac{a\theta}{\mu M \tilde{k}_s}\frac{2\vartheta_s}{\sin 2|\vartheta_s - \varphi|}. \tag{27}$$

By using the values of θ_S obtained above in limiting cases, one can make the $\delta_S = \delta_S(k_1)$ relation specific. We note that although $\delta_S(k_1)$ repeats the singularities of θ_S, it does not always become infinite on approach to the values of k_1 at which a uniform state occurs: for example, when $\varphi = \pi/2$ and $k_1 \to -\sigma^2|k_2|$ $(k_2 \gtrless 0)$ from larger values of k_1:

$$\delta_s \to a\theta/\mu M \tilde{k}_s.$$

Another characteristic of the nonuniformity of the state $\theta(x)$ is the quantity δ_V, which describes the passage of the solution to the asymptotic behavior, $\theta(x) \to \theta(\infty)$, for $x \gg \delta_S$. According to (7)

$$\delta_V = (2C)^{1/2}[f_V''(\vartheta_\infty)]^{-1/2}. \tag{28}$$

From this expression it is clear that δ_V becomes infinite at those values of k_1 at which there occurs a change of behavior within the volume. As is evident from the preceding, the dependence on x in $\theta(x)$ does not disappear. We consider as an example of such a case: $k_1 = 0, k_2 < 0, 0 < \varphi \neq \pi/2$. Using (7) and (5′), we have

$$\operatorname{ctg}\vartheta - \operatorname{ctg}\vartheta_s = x/\tilde{\delta}, \quad \tilde{\delta} = (C/|k_2|)^{1/2}. \tag{29}$$

When $x \gg \tilde{\delta}$, $\theta(x) \approx \tilde{\delta}/x$. As was to be expected,[4] because of the infiniteness of the correlation radius the transition to the equilibrium (volume) value occurs according to a power law.

5. THE ROLE OF FLUCTUATIONS

Surface phase transitions possess singularities caused by their two-dimensional nature. In particular, the fluctuational corrections have an unusual structure. In order to demonstrate this, we shall calculate the fluctuations of the angle $\theta(x)$ near a point of surface phase transition of second order, when $k_1 \lesssim -\sigma^2 k_2$ $(k_2 > 0, \sigma > 1$, $\varphi = \pi/2$, Fig. 7b). The fluctuation $\delta\theta$ of the angle obeys the following equation:

$$\Delta\delta\vartheta - k_1\delta\vartheta/C = 0, \quad \delta\vartheta \to 0 \quad \text{as} \quad x \to \infty. \tag{30}$$

Since at the boundary

$$\frac{d}{dx}\delta\vartheta|_{x=0} = -\frac{k_s}{C}\delta\vartheta|_{x=0}, \tag{31}$$

therefore $\delta\theta(\mathbf{r}) = \delta\theta(\rho)e^{-\gamma x}$, where $\gamma = k_S/C$ and where $\delta\theta(\rho)$ is the solution of the two-dimensional equation

$$\Delta_2\delta\vartheta(\rho) + (\gamma^2 - |k_1|/C)\delta\vartheta(\rho) = 0. \tag{32}$$

Hence the correlation radius of the fluctuation is

$$\rho_c = \varkappa_c^{-1}, \quad \varkappa_c^2 = (|k_1| - \sigma^2 k_2)/C,$$

that is,

$$\rho_c = [C/(|k_1| - \sigma^2 k_2)]^{1/2}.$$

The fluctuational part of the thermodynamic potential, after integration over the depth, takes the form

$$\delta\Omega_{fl} \approx (|k_1| - \sigma^2 k_2)(M^2 CS/2k_s)(\delta\vartheta_s)^2, \tag{33}$$

where S is the area of the surface of the body and where $\delta\theta_S$ is the value of the fluctuation of the angle on the surface $(x = 0)$. Hence

$$\langle(\delta\vartheta_s)^2\rangle = Tk_s/SM^2C(|k_1| - \sigma^2 k_2), \tag{34}$$

and the mean square fluctuation, averaged over the correlation area $S_{cor} \approx \rho_c^2$, is

$$\langle(\delta\vartheta_s)^2\rangle = Tk_s/M^2C^2 \approx (T\mu M/\theta^2)k_s. \tag{35}$$

We point out the fact that $\langle(\delta\theta_S)^2\rangle$ does not tend to zero on approach to the transition point [in the case of volume transitions, the square of the averaged fluctuation over the correlation volume is proportional to $\tau^{1/2}$, where $\tau = (\theta_c - T)/\theta_c$; see Ref. 2, §146]. According to (35) and (18), the fluctuations are critical when

$$||k_1| - \sigma^2 k_2| \leqslant (T\mu M/\theta^2)\tilde{k}_s k_2(\sigma^2 - 1) \tag{36}$$

or

$$\left| |k_1| - \tilde{k}_s\frac{\mu M}{\theta} \right| \leqslant \frac{T}{\theta}\tilde{k}_s\left(\tilde{k}_s - k_2\frac{\mu M}{\theta}\right). \tag{36′}$$

This condition is considerably more exacting (the fluctuational range is broader) than the Levanyuk-Ginzburg condition formulated above (see §1). Approach of $\tilde{k}_S$ to $(k_2\mu M/\theta)^{1/2}$ diminishes the role of fluctuations, since for $k_S = (k_2\mu M/\theta)^{1/2}$ the transition under investigation becomes transformed to a transition of the first kind (cf. Fig. 7a and b).

6. CONCLUSION

The problem solved here is similar to problems in the calculation of domain structures during spin-orientation transitions (see the bibliography to Chapter I in the book of Belov *et al.*[1]). The specific characteristic of the present treatment is the introduction of the surface energy, which makes the value of the direction of the magnetic moment at the boundary (the angle θ_S) an additional parameter characterizing the state of the magnet. Apparently there are not at present sufficiently definite experimental data with which to compare the results obtained here. The author hopes that the present publication will stimulate, one the one hand, investigations of reorientational transitions on the basis of surface characteristics (for example, on the basis of reflection of light); and on the other, the development of methods of study of the surface that use the state diagram of magnets near reorientational transitions.

[1)] It has been assumed (and this is important!) that the magnetic moment both on the surface and in the interior is parallel to the plane of the specimen surface. This means that the total anisotropy energy has the following structure:

$$f_V(\vartheta, \chi) = k_1^* \sin^2\vartheta \cos^2\chi - k_1^{**} \sin^2\vartheta - k_2 \sin^4\vartheta, \quad k_1^* > 0, \tag{1'}$$

χ is the angle between the magnetic moment and the direction of the normal to the surface. If the surface energy also attains a minimum for $\chi = 0$, then $\chi(x) \equiv 0$ and $f_V(\theta) = f_V(\theta, \chi = 0)$, $k_1 = k_1^{**} - k_1^*$.

[2)] We note a curious detail: if θ_∞ corresponds not to a minimum of the function $f_V(\theta)$ but to its smallest value (this is so in reorientation transitions), then $d\theta/dx$ vanishes at a finite distance x_m from the boundary:

$$\frac{x_m}{C^{1/2}} = \operatorname{sign}(\vartheta_\infty - \vartheta_S) \int_{\vartheta_S}^{\vartheta_\infty} \frac{d\vartheta}{[f_V(\vartheta) - f_V(\vartheta_\infty)]^{1/2}},$$

and this means that the interior of a specimen whose dimension is larger than $2x_m$ does not feel the surface at all. If $f'_V|_{\theta=\theta_\infty} = 0$, then $x_m = \infty$.

[3)] It is not obligatory to detect narrowing of the hysteresis loop on the basis of the $\theta_S = \theta_S(k_1)$ relation. The surface energy shifts the lability point, i.e. changes the hysteresis loop $\theta_\infty = \theta_\infty(k_1)$.

[1] K. P. Belov, A. K. Zvezdein, A. M. Kadomtseva, and R. Z. Levitin, Orientatsionnye perekhody v redkozemel'nykh magnetikakh (Orientational Transitions in Rare-Earth Magnetic Materials), Nauka, 1979.

[2] L. D. Landau and E. M. Lifshitz, Statisticheskaya fizika (Statistical Physics, Nauka, 1976, Part 1 (transl. of 1964 edition, Pergamon Press and Addison-Wesley, 1969).

[3] L. D. Landau and E. M. Lifshitz, Élektrodinamika sploshnykh sred (Electrodynamics of Continuous Media), Gostekhizdat, 1957 (transl., Pergamon Press and Addison-Wesley, 1960).

[4] M. I. Kaganov and N. S. Karpinskaya, Zh. Eksp. Teor. Fiz. 76, 2143 (1979) [Sov. Phys. JETP 49, 1083 (1979)].

Translated by W. F. Brown, Jr.

Giant spin splitting of excitonic states in the hexagonal crystal CdSe:Mn

A. V. Komarov, S. M. Ryabchenko, Yu. G. Semenov, B. D. Shanina, and N. I. Vitrikhovskiĭ

Institute of Physics, Ukrainian Academy of Sciences
and Institute of Semiconductors, Ukrainian Academy of Sciences

(Submitted 25 April 1980)
Zh. Eksp. Teor. Fiz. **79**, 1554–1560 (October 1980)

The effect of giant spin splitting of excitonic states in semiconductors with magnetic impurities was first observed for the hexagonal crystal CdSe:Mn. A theoretical explanation is presented for those peculiarites of the effect which are connected with the anisotropy of the crystal. Comparison with experiment was used to determine the band-structure parameters $\Delta_1 = 46 \pm 3$, $\Delta_2 = 137 \pm 1$, and $\Delta_3 = 140.6 \pm 0.3$ meV. It is shown that in CdSe:Mn, just as in cubic semiconductors, the exchange interaction with the magnetic impurities is ferromagnetic for the electrons of the conduction band and antiferromagnetic for the electrons of the valence band. The exchange constants are of the same order of magnitude as for the crystals CdTe:Mn, ZnTe:Mn, and ZnSe:Mn.

PACS numbers: 71.35. + z, 71.70. – d

INTRODUCTION

The effects of giant spin splittings of electronic (and correspondingly excitonic) states in II–VI semiconductors with magnetic impurities or else in the solid solutions $A^{II}_{1-x}M_xB^{VI}$ (here M is a 3*d* ion) were recently observed and investigated in the cubic crystals CdTe:Mn,[1-3] ZnTe:Mn,[4] ZnSe:Mn, and ZnSe:Fe.[5] A phenomenological theory of the effect was considered in Refs. 1, 2, and 4 on the basis of the concept of carrier-impurity exchange interaction. Values were obtained for the energies and for the probabilities of the transitions into the excitonic states. A microscopic theory of the carrier–impurity exchange interaction was previously proposed[6] for semiconductors with cubic symmetry, and the experimentally observed[1-5] difference between the signs of the constants of the exchange interaction of the conduction electrons I_{cM} and the valence electrons I_{vM} with the 3*d* ions was explained. No such effects in noncubic crystals were previously investigated either experimentally or theoretically.

We present here the results of an experimental investigation of giant spin splittings of excitonic states in hexagonal CdSe:Mn, as well as a theory that explains the observed effects.

 0038-5646/80/100783-05$02.40