Surface magnetoelectric effects and double electric-magnetic layers in degenerate magnetic semiconductors

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Abstract. The surface magnetization of degenerate ferromagnetic and antiferromagnetic semiconductors is investigated. It can appear due to a surface potential acting on the charge carriers or to an external electric field directed normally to the semiconducting film. In the first case a double electric–magnetic layer arises at the surface. The difference in magnetizations inside this layer is maximally pronounced close to T_C. An external field reduces the total magnetization of ferromagnetic semiconductors (the antimagnetoelectric effect) and produces magnetization of initially non-magnetized antiferromagnetic semiconductors. Unlike the well known magnetoelectric effect, such a surface magnetoelectric effect exists independently of the symmetry of the crystal.

1. Introduction

Surface magnetism has been a subject of physical investigation for a long time (see, e.g., review articles [1–3]). Recently, interest in this phenomenon has greatly increased due to the fact that it plays an important role in the properties of colossal-magnetoresistance materials when used as thin films. There are many reasons for which the surface properties should differ from the bulk ones. In the insulating Heisenberg systems this difference can be caused by the very fact of breaking bonds between atoms at the surface, as well as by a difference between the exchange couplings at the surface and in the bulk of a crystal. Usually this leads to a reduced surface magnetization as compared to the bulk one. For example, the existence was discovered of a paramagnetic layer on the surface of the ferromagnetic semiconductor EuO well below the Curie point [4].

But in conducting magnetic systems where the conduction electrons realize an indirect exchange between localized magnetic moments, the electron surface density can exceed the bulk one. For this reason the surface indirect exchange coupling can be stronger than the bulk one. For example, in ferromagnetic Gd the surface Curie point is 310 K whereas the bulk one is only 292.5 K [5]. Moreover, in conducting systems the surface magnetic ordering of antiferromagnetic crystals can transform into ferromagnetic ordering: in Cr the surface Curie point is 780 K whereas the bulk Néel point is 312 K [6]. In EuO samples containing several per cent of the donor impurity Gd, the surface magnetization turns out to be much higher than that for the undoped samples. Also, the surface paramagnetism disappears also after adsorption of Cs acting as a surface donor impurity [4, 7].

The aim of the present paper is to investigate theoretically specific features of the surface magnetization of the group of degenerate magnetic semiconductors, to which, in

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particular, colossal-magnetoresistance materials of the lanthanum manganite type belong. The consideration is based on the fact that the very existence of the surface or of an external electric field produces a non-uniform charge-carrier distribution. As the carriers realize the indirect exchange between magnetic atoms, a non-uniformity in their distribution changes the magnetic properties of the system close to the surface.

One should discuss the cases of doped antiferromagnetic and ferromagnetic semiconductors separately. One should also keep in mind that the charge carriers tend to establish the ferromagnetic ordering [8]. For this reason there is a tendency towards separation of antiferromagnetic semiconductors into an insulating antiferromagnetic phase and a highly conductive ferromagnetic phase [9, 10]. For thin films this manifests itself in the appearance of a layered structure, with the surface layers being ferromagnetic or antiferromagnetic, depending on the sign of the surface electron potential [11]. But the phase separation is possible only in systems for which the Néel points are sufficiently low.

In the non-phase-separated antiferromagnetic semiconductors, another scenario is realized. The RKKY theory of indirect exchange is inapplicable to them, and for this reason non-trivial effects become possible. The collinear antiferromagnetic ordering is stable up to a certain critical density n_A, and, starting from a still larger density n_F, the ferromagnetic ordering becomes stable. In the range between n_A and n_F, the energy of the canted antiferromagnetic ordering is lower than the energies of both collinear states just mentioned, though one cannot guarantee that the canted ordering is absolutely stable. For example, some other state with non-saturated magnetization might be more energetically favoured than the canted state.

If the mean density in the crystal is less than n_A, then the surface potential can increase the surface density (for example, this may occur after adsorption of certain species). As a result, magnetized layers arise on the surface of an antiferromagnetic crystal. It should be noted that surface canted antiferromagnetic ordering was observed in systems for which bulk canted ordering is impossible [12].

The fact that the antiferromagnetic ordering becomes unstable at a finite charge-carrier density makes it possible to observe a specific surface magnetoelectric effect. If one applies an external electric field normally to a plane-parallel antiferromagnetic plate with the mean charge-carrier density n less than n_A, then on one of its surfaces the carrier density may exceed n_A, and this surface becomes magnetized. On the other hand, the opposite surface with reduced density remains unmagnetized. Thus, the film as a whole becomes magnetized by an external electric field.

To clarify this question, one should point out that usually one considers the magneto-electric effect in uniform electric fields and infinite-size samples. Then a magnetization linear in the external electric field arises if the crystal possesses special symmetry properties [13]. As was pointed out in reference [8], at finite temperatures, in conducting infinite-size crystals, a non-uniform electric field causes the magnetoelectric effect independently of the crystal symmetry. Here it will be shown that, in conducting finite-size samples, the total magnetization also arises under a uniform electric field, but this magnetization is quadratic in the field strength.

As for the ferromagnetic semiconductors, change in the electron density always leads to change in the local magnetization at finite temperatures. The local magnetization and charge-carrier density are related to each other in a self-consistent manner: the local conduction electron (or hole) density is higher for higher local magnetization, and vice versa [8]. One should also take into account the fact that the non-uniform charge-carrier distribution close to the surface produces electrostatic forces which can be reduced by the screening of this distribution.

As a result, a double magnetic–electric layer arises close to the surface. It consists of two layers with opposite electric charges and different magnetizations. Depending on the sign of the electron surface potential of the two layers forming the double layer, the layer closest to the surface can be more strongly or more weakly magnetized. In the latter case the other ('subsurface') layer should be the most strongly magnetized one in the crystal. The magnetization effect is most pronounced in the vicinity of the Curie point. When $T \to 0$ or $T \to \infty$ the difference in the magnetizations of both of the layers vanishes, and only an electric double layer remains on the surface.

An external electric field changes the magnetization of a ferromagnetic semiconductor: at finite temperatures the surface of the film with increased charge-carrier density is magnetized more strongly, and the opposite surface is magnetized more weakly than the bulk. But, unlike the case for an antiferromagnetic semiconductor, the electric field reduces the total magnetization. Hence, one may speak of the antimagnetoelectric effect in this case. As in the preceding case, the effect is maximal in the vicinity of T_C.

2. Magnon spectra and stability conditions for collinear structures

In this section some general results obtained by the author previously, which are necessary for constructing the present theory, will be summarized. The standard s–d model is used to describe the electric and magnetic properties of magnetic semiconductors:

$$H = \sum E_k a_{k\sigma}^* a_{k\sigma} - \frac{A}{N} \sum (s \cdot S_g)_{\sigma,\sigma'} \exp[i(k - k') \cdot g] a_{k\sigma}^* a_{k'\sigma'} - \frac{I}{2} \sum S_g \cdot S_{g+\Delta} \quad (1)$$

where $a_{k\sigma}^*$, $a_{k\sigma}$ are the s-electron operators corresponding to the conduction electrons or holes with the quasi-momentum k and spin projection σ, s the s-electron spin operator, S_g that of the d spin of atom g, N the number of atoms in the crystal, Δ the vector connecting the first-nearest neighbours, and z their number. The first term in equation (1) is the s-electron kinetic energy, the second is the s–d exchange energy, and the third is the direct exchange interaction between d spins. For the sake of definiteness, the s–d exchange integral A is assumed to be positive.

Two limiting cases will be considered: the double exchange when the s-electron bandwidth W is small compared to the energy AS of the s–d exchange, where S is the d-spin magnitude, and the opposite case of a 'weak' s–d coupling, $W \gg AS$. An additional condition appropriate for magnetic semiconductors will also be used in the latter case: $\mu < AS$ where μ is the Fermi energy. This reflects the relatively small charge-carrier density in semiconductors, and, in the case of the ferromagnetic ordering, corresponds to the complete spin polarization of the s electrons instead of the spin depolarization assumed in the RKKY theory of indirect exchange. The latter condition means, in particular, that, generally speaking, the RKKY theory is inapplicable to magnetic semiconductors.

The corresponding theory developed by the author for magnetic semiconductors is described in the book [8]. The bulk magnon frequencies for a ferromagnetic semiconductor are given by the expressions

$$\omega_q = \omega_q^d + \omega_q^i \quad (2)$$

$$\omega^d = J(1 - \gamma_q) \qquad J = ISz \qquad \gamma_q = \frac{1}{z} \sum_\Delta \exp(iq \cdot \Delta) \quad (3)$$

$$\omega_q^i = \frac{Aq^2 v}{2(q^2 + q_0^2)} \qquad q_0^2 = 2mAS \qquad \text{for } W \gg AS \quad (4)$$

$$\omega_q^i = J_i(1 - \gamma_q) \qquad J_i = \frac{ztv}{2S} \qquad \text{for } W \ll AS. \qquad (5)$$

Here $v = na^3$ the number of s electrons per magnetic atom, a the lattice constant, and $\hbar = 1$. The s-electron energy is assumed to be expressed through their effective mass m or the hopping integral t in a standard manner:

$$E_k = -zt\gamma_k \cong -zt + \frac{k^2}{2m}. \qquad (6)$$

In deducing equations (2)–(5), the inequality $S \gg 1$ was also used.

In the case of collinear antiferromagnetic ordering, when the spin polarization of the s electrons is absent, for $W \gg AS$ the expression for the magnon frequencies coincides with the RKKY expression:

$$\omega_q = \sqrt{(K_Q - K_q)(K_Q - K_{Q+q})} \qquad (Q = \pi/a, \pi/a, \pi/a) \qquad (7)$$

$$K_q = J\gamma_q - \frac{A^2 S}{2N} \sum \frac{n_k - n_{k+q}}{E_k - E_{k+q}} \qquad n_k = \Theta(\mu - E_k)$$

where $\Theta(x)$ is the Heaviside step function. At small electron densities, the stability of the antiferromagnetic ordering is a consequence of J being negative. The loss of the stability begins when the magnon frequencies turn out to be imaginary at wave vectors q close to **0** and **Q**. Then one obtains from equations (6) and (7) the density corresponding to the antiferromagnetic instability:

$$v_A = (3\pi^2)^2 \left(\frac{16|J|}{3Aq_0^2 a^2} \right)^3. \qquad (8)$$

As follows from equations (2) and (4), the ferromagnetic magnons become stable starting from

$$v_F = \frac{4|J|}{A} = \frac{3ASv_A}{4\mu} \qquad \mu = \frac{(3\pi^2 n)^{2/3}}{2m} \qquad (9)$$

i.e., in fact, for $\mu < AS$ a range of densities exists over which both the antiferromagnetic and the ferromagnetic orderings are unstable, and one may expect the existence of an intermediate ordering with unsaturated magnetization.

Now the case of the double exchange will be discussed. Unfortunately, the magnon spectrum has not been found for the antiferromagnetic state yet. Moreover, as the motion of the charge carrier over the crystal is always accompanied with rotations of the d spins (the magnetic string, or quasi-oscillator, effects [14]), it may even be the case that the magnons cannot be separated from the charge carriers. For this reason another approach will be used to prove that the antiferromagnetic ordering is stable up to some finite carrier density.

With this aim, the canted antiferromagnetic ordering will be considered, with 2θ being the angle between the sublattice moments. Then, according to [8], the charge-carrier spectrum consists of two subbands with the dispersion relations

$$E_\pm(k) = -zt_\pm \gamma_k \qquad (10)$$

$$t_\pm = \frac{t(\sqrt{1+y^2} \pm y)}{\sqrt{2S+1}} \qquad y = \frac{M}{\sqrt{2S+1}} \qquad M = S\cos\theta.$$

The ground-state energy of this state, consisting of exchange and kinetic contributions, is found from the expression

$$E_{ek} = -3IS^2 N \cos 2\theta + \sum E_\pm(k)n_\pm(k) \qquad (z = 6) \qquad (11)$$

with allowance made for the independence of the total carrier number of θ. Minimizing equation (11) with respect to M, one finds, for small carrier numbers per magnetic atom $\nu = n/N$,

$$-12IM - 6\sum_{\pm} \nu_{\pm} \frac{\mathrm{d}t_{\pm}}{\mathrm{d}M} = 0 \tag{12}$$

where the relative carrier densities in both subbands are determined from the condition of equality of the chemical potentials in them, i.e., from

$$t_{+}[-6 + (6\pi^2\nu_{+})^{2/3}] = t_{-}[-6 + (6\pi^2\nu_{-})^{2/3}]. \tag{13}$$

Due to the small ν-values, the following inequality holds:

$$R(\nu) \equiv 12(3\pi^2\nu)^{-2/3} \gg 1.$$

For small M one obtains from equations (10) and (13), with allowance made for this inequality,

$$\nu_{+} - \nu_{-} \simeq \nu\left[\frac{3}{4}Ry - \frac{1}{32}R^3y^3\right]. \tag{14}$$

Thus the total energy can be written in the form

$$E_{ek}/N = K_0 + K_2M^2 + K_4M^4 \tag{15}$$

$$K_0 = 3IS^2 - \frac{6t\nu}{\sqrt{2S+1}} + \frac{3(3\pi^2)^{2/3}t\nu^{5/3}}{5\sqrt{2S+1}}$$

$$K_2 = -6I - \frac{3t\nu R(\nu)}{4(2S+1)^{3/2}}$$

$$K_4 = \frac{3t\nu R^3(\nu)}{16(2S+1)^{5/2}}.$$

A similar expansion can be written down in the opposite case of $W \gg AS$.

Expression (15) resembles the Landau expansion for the free energy in the phase transition theory. The coefficient K_4 is always positive. As $I < 0$, the coefficient K_2 is positive at small ν and negative for ν sufficiently large. Hence, at such densities the collinear antiferromagnetic ordering is unstable. It loses its stability at

$$\nu_A = \left(\frac{\pi}{3}\right)^4 \left[\frac{2|I|(2S+1)^{3/2}}{t}\right]^3 \sim \frac{T_N^3}{W(2S)^{3/2}} \tag{16}$$

where T_N is the Néel temperature of the undoped crystal which should be small as compared with the bandwidth W.

As follows from equations (2), (3), and (5), the collinear ferromagnetic ordering becomes stable at

$$\nu_F = \frac{2|I|S^2}{t} \sim \frac{T_N}{W} \tag{17}$$

Because of the inequality $T_N \ll W$, a range of densities $[n_A, n_F]$ exists over which both the collinear antiferromagnetic and the ferromagnetic orderings are unstable, and the canted antiferromagnetic ordering has energy lower than that of the collinear antiferromagnetic ordering.

It should be noted that the idea of the possibility of canted antiferromagnetic ordering for double exchange was first advanced by de Gennes [15]. But only classical spins were considered in that paper, and for this reason the quantity ν_A vanished there. Hence, in some sense, the magnetoelectric effect considered below is essentially quantum mechanical.

The boundary density for the collinear ferromagnetic ordering obtained in reference [15] coincides with equation (17).

The calculations presented above do not necessarily imply that the canted state is really stable. Possibly, some other state intermediate between the ferromagnetic and anti-ferromagnetic states has still lower energy. If this state is partially magnetized, equation (15) can be considered as phenomenological under the assumption that $K_4 > 0$, and K_2 changes its sign at a certain ν_A. Then at densities close to ν_A, the magnetization should be

$$M \sim \sqrt{\nu - \nu_A}. \tag{18}$$

Finally, expressions for the s-electron energy renormalized due to the interaction with the magnons can be presented for the ferromagnetic semiconductors [8]. In the temperature range $T_C/S \ll T \ll T_C$ (where T_C is the Curie point), they are as follows (see equation (5)):

$$E_k^s = -\frac{AM}{2} - zt\gamma_k \qquad M = S - \frac{T}{N}\sum\frac{1}{\omega_q} \qquad \text{at } W \gg AS \tag{19}$$

$$E_k^s = -\frac{AS}{2} - zt\Lambda\gamma_k \qquad \text{at } W \ll AS \tag{20}$$

$$\Lambda = 1 - \frac{T}{2SN}\sum\frac{(1 - \gamma_q)}{\omega_q} = 1 - \frac{T}{2S(J + J_i)}. $$

3. Double electric–magnetic layers in ferromagnetic semiconductors

We begin with the simpler case of the ferromagnetic semiconductor. A conducting crystal with a simple cubic structure is considered, its shape being that of a thin film limited by the $x = \pm L$ planes. Here the case in which the donor (acceptor) impurity positions are frozen will be considered. The impurity is assumed to be distributed uniformly over the crystal. The electron (hole) potential energy close to the surface is assumed to be given by

$$U_e(x) = u_e\frac{\cosh\alpha x}{\cosh\alpha L} \qquad (\alpha L \gg 1) \tag{21}$$

where $1/\alpha$ is the surface potential length which is assumed to amount to several lattice constants a. In addition to this potential, the electron energy depends also on the local magnetization. It is determined from equations (18) or (19), in which the x-dependent magnon frequencies should be substituted. They are given by equations (2)–(5) generalized for the x-dependent s-electron density $n(x)$:

$$\omega_q = \omega_q^d + b_q n(x) \qquad (b_q > 0) \tag{22}$$

where the meaning of the notation b_q is obvious from equations (4) and (5). Such a local coupling between the magnon frequency and the density takes place if the length over which the density changes markedly is large compared with the typical magnon wavelength, which is the lattice constant under the above-mentioned conditions. On the other hand, the typical length for the electron density is the length of the surface potential $1/\alpha$ or the screening length $1/\kappa$, which could be considered as large compared to a.

The electron density distribution is found from the condition of constant electrochemical potential together with the Poisson equation. In the case where $W \gg AS$, the former has the form

$$Cn^{2/3}(x) + U_e(x) + e\phi(x) - AM(x)/2 = \text{constant} \qquad C = \frac{(6\pi^2)^{2/3}}{2m} \tag{23}$$

where m is the electron effective mass. In writing equation (23), the assumption was made that all of the electrons are spin polarized, which is typically the case for ferromagnetic

semiconductors in the spin-wave region. Furthermore, ϕ is the electrostatic potential arising due to the non-uniform electron distribution. The latter should be determined from the Poisson equation

$$\frac{\mathrm{d}^2\phi}{\mathrm{d}x^2} = -\frac{4\pi e}{\epsilon}\delta n(x) \qquad \delta n(x) = n(x) - n_0 \tag{24}$$

where n_0 is the compensating impurity density and ϵ is the dielectric constant. Its boundary conditions should express the sample electroneutrality:

$$\frac{\mathrm{d}\phi(L)}{\mathrm{d}x} = \frac{\mathrm{d}\phi(-L)}{\mathrm{d}x} = 0. \tag{25}$$

We shall begin with the standard linearization procedure for equation (23), considering $\delta n(x)$ as small compared to n_0. Then one obtains from equations (23)–(25)

$$\delta n(x) = -\frac{n'}{1-\Gamma}[U_e(x) + e\phi(x)] \qquad n' = \mathrm{d}n_0/\mathrm{d}\mu \tag{26}$$

$$\phi(x) = \frac{u_e\kappa^2}{e(\alpha^2 - \kappa^2)\cosh\alpha L}\left(\cosh\alpha x - \frac{\alpha\sinh\alpha L\cosh\kappa}{\kappa\sinh\kappa L}\right) \tag{27}$$

where the screening length $1/\kappa$ and the magnetoelectric parameter Γ are given by the following expressions:

$$\kappa^2 = \frac{4\pi e^2 n'}{\epsilon(1-\Gamma)} \tag{28}$$

$$\Gamma = \frac{3n^{1/3}A}{2C}\frac{\mathrm{d}M}{\mathrm{d}n} = \frac{3n^{1/3}AT}{2CN}\sum\frac{b_q}{\omega_q^2} \qquad b_q = \frac{Aq^2a^3}{2(q^2+q_0^2)} \tag{29}$$

(equation (22) is used).

A similar calculation can be carried out for the case where $W \ll AS$. With allowance made for (20) and (23), the condition of constant electrochemical potential takes the following form here:

$$C\Lambda(x)n^{2/3}(x) + U_e(x) + e\phi(x) - zt\Lambda(x) = \text{constant}. \tag{30}$$

Due to the s-electron density being small, the renormalization of the hopping integral is not taken into account here. Then, repeating the preceding calculations, one obtains again equations (27) and (28), but equation (29) should be replaced by

$$\Gamma = \frac{3n^{1/3}zt}{2C}\frac{\mathrm{d}\Lambda}{\mathrm{d}n} = \frac{3n^{1/3}Tta^3}{4SC(J+J_i)^2}. \tag{31}$$

As follows from equations (26) and (27), at $x = 0$ the change in the density δn is exponentially small. If $\alpha L \gg 1$, $\kappa L \gg 1$, and $\alpha > \kappa$, then, close enough to the surface, the following expression is valid:

$$\delta n = -\frac{n'u_e\alpha}{(1-\Gamma)(\alpha^2-\kappa^2)}[\alpha\exp(-\alpha y) - \kappa\exp(-\kappa L)] \qquad y = |L-x|. \tag{32}$$

As seen from equation (32), at the surface $y = 0$ the sign of δn is opposite to the sign of u_e, as should be the case. But δn changes its sign over a length of

$$l_s = \frac{1}{\alpha-\kappa}\ln\frac{\alpha}{\kappa}. \tag{33}$$

The excess charge of the opposite sign disappears over a length l_{ss} of order $1/\kappa$, which is the effective thickness of the subsurface charge layer.

According to equations (2) and (19), at finite temperatures the magnetization increases with the electron density. Hence, for $u_e < 0$ the surface layer is charged negatively or positively if the charge carriers are electrons or holes, respectively. But in both cases its magnetization is higher than that of the subsurface layer. In contrast, for $u_e > 0$ the sign of the charging of the surface layer is opposite, and its magnetization is lower than that of the subsurface layer. This shows the tendency towards formation of a paramagnetic layer on the surface of the ferromagnetic system.

It should be noted that the electric double layer exists at all temperatures, including $T = 0$. But the magnetic double layer exists only at finite temperatures. At $T = 0$ the magnetization is everywhere maximal, so the magnetic double layer cannot exist. According to equations (29) and (31), in the spin-wave region the parameter Γ increases with temperature. Hence, according to equations (29), (31), and (33), the difference in magnetization of the layers forming the double layer, as well as the difference in its geometrical parameters l_s and l_{ss}, increase with temperature. But for $T \to \infty$ the magnetization disappears everywhere. Hence, the local magnetization cannot increase as a result of an increased electron density, and the magnetic double layer does not appear, either. This means that the magnetic double layer should be most pronounced at temperatures of order T_C.

So far, only the case of small δn has been discussed. According to equation (27), the excess surface electron density is of order u_e/μ. If u_e is sufficiently large and positive, a depletion layer should arise on the surface. For semiconductors with μ of the order of several tenths of an eV, this situation is quite typical. In such cases the surface paramagnetic layer should be especially pronounced.

4. Surface layers at mobile impurity atoms

So far, it has been assumed that the positions of the impurity atoms are frozen. Now the case of mobile impurities will be discussed, in which not only the electrons but also the compensating impurity atoms are mobile at temperatures for which a magnetic ordering exists (for example, oxygen in HTSC cuprates; see the review article [10]). Then one should take into account not only the surface potential for the electrons (21) but also the surface potential $U_i(x)$ for the compensating impurity, which differs from equation (21) by the replacement of u_e by u_i. The condition for the electrochemical impurity potential to be constant is written down with account taken of the requirement for the impurity-ion system to be non-degenerate:

$$T \ln v p(x) - e\phi(x) + U_i(x) = \text{constant} \qquad v = a^3 \tag{34}$$

where $p(x)$ is the impurity density. Linearizing (34) with respect to $\delta p(x) = p(x) - p_0$, one obtains the Poisson equation in the form

$$\frac{\mathrm{d}^2\phi}{\mathrm{d}x^2} = \kappa_i^2 \phi + k \frac{\cosh \alpha x}{\cosh \alpha L} \tag{35}$$

$$\kappa_i^2 = \frac{4\pi e^2}{\epsilon}\left(\frac{n'}{1-\Gamma} + \frac{n_0}{T}\right) \qquad k = \frac{4\pi e}{\epsilon}\left(\frac{u_e n'}{1-\Gamma} - \frac{u_i n_0}{T}\right).$$

In solving equation (35), one should keep in mind that the contributions of the impurity to κ^2 and k are $\sim \mu/T$ times larger than those of the electrons. For this reason one may assume the inequality $\kappa > \alpha$. Then one obtains, close to the surface,

$$\delta n = -\frac{n' u_e}{1-\Gamma}\exp(-\alpha y) \qquad \delta p = -\frac{n_0 u_p}{T}\exp(-\alpha y). \tag{36}$$

As seen from equations (36), in the spin-wave region, with increase in temperature, the difference between the surface and bulk electron densities increases. Hence, the surface magnetization increases in absolute value, but its typical length here is only $1/\alpha$ and not $1/\kappa$. In contrast, the surface surplus or deficiency in the impurity density decreases with temperature. This result is valid for all of the temperatures, and not only for the spin-wave region. Well above the Curie point, the surface electron density becomes temperature independent.

5. The surface magnetoelectric effect

First, the magnetoelectric effect will be investigated for a ferromagnetic semiconductor with frozen impurity. A uniform electrostatic field $\boldsymbol{F}$ is applied perpendicularly to the film surface. In this case, to simplify the treatment, one may put $U_e(x) = 0$, and the boundary conditions for equation (24) take the form

$$\frac{\mathrm{d}\phi(\pm L)}{\mathrm{d}x} = F. \tag{37}$$

Then one obtains

$$\phi(x) = \frac{F \sinh \kappa x}{\sinh \kappa L} \tag{38}$$

$$\delta n(x) = -\frac{q \sinh \kappa x}{\cosh \kappa L} \qquad q = \frac{F \kappa \epsilon}{4\pi e}. \tag{39}$$

One sees from equation (39) that at one surface the electric field increases the electron density and, hence, the magnetization. At the other surface the magnetization is reduced by the electric field. Using equations (19) and (20), one can find also the change in the average magnetization induced by the electric field:

$$\langle M \rangle = M_0 - \frac{F^2 T \kappa \epsilon P}{(4\pi e)^2 L} \tag{40}$$

$$M_0 = S - \frac{T}{(2\pi a)^3} \int \frac{\mathrm{d}^3 q}{\omega_q^0} \tag{40a}$$

$$P = \frac{1}{(2\pi a)^3} \int \frac{b_q^2 \, \mathrm{d}^3 q}{(\omega_q^0)^3} \qquad \omega_q^0 = \omega_q^d + b_q n_0$$

where the symbol $\langle \cdots \rangle$ denotes averaging over the sample.

As seen from equation (40), the external electric field reduces the total magnetization. This 'antimagnetoelectric' effect is quadratic in the field strength and disappears on increase of the film thickness, being inversely proportional to it.

A real magnetoelectric effect is possible in doped antiferromagnetic semiconductors with the charge-carrier density at which the collinear antiferromagnetic ordering is stable ($\nu < \nu_A$). Then, under the electric field, the density at one of the surfaces may exceed ν_A, whereas everywhere else it remains below ν_A. The typical thickness of the layer with $\nu > \nu_A$ for which the magnetization is non-zero must be of the order of the screening length. Hence, the total magnetization should vanish with increasing film thickness as $1/L\kappa$.

Certainly, the magnetization should depend on the coordinate x, which makes the problem non-local. To treat it, a variational procedure will be used. Continuous changes in the carrier density on moving off from both of the surfaces will be approximated by step-like changes in the density. Moreover, it will be assumed that the widths of the layers

on both sides of the film are equal to each other, which assumes that the field-induced change in carrier density is not very large, and that the depletion layer does not arise. Then the s-electron density is taken to be equal to $n_0 + \lambda$ between L and $L - l$, to n_0 between $L - l$ and $-L + l$, and to $n_0 - \lambda$ between $-L + l$ and $-L$. The relation between the surplus density λ and the thickness of the layers l is found from the condition that the total electric field should vanish outside the surface layers. This gives

$$\lambda l = \frac{\epsilon F}{4\pi e}. \tag{41}$$

Hence, l can be considered as a variational parameter. The magnetized ordering is assumed to be canted antiferromagnetic, with the canting angle θ as another variational parameter.

Only the case of the double exchange with $W \ll AS$ will be treated. For $l \gg a$ the total energy of the inhomogeneous system can be represented in the form

$$E_{tot} = E_{ek}^{(-L,-L+l)} + E_{ek}^{(-L+l,L-l)} + E_{ek}^{(L-l,L)} + \frac{e}{2} \int d^3r \ \phi(x)[n(x) - n_0]. \tag{42}$$

The first three terms in (42) represent the exchange–kinetic energy (11) in the corresponding x-ranges. In the case of the collinear antiferromagnetic ordering, with allowance made for equation (41), the s-electron kinetic energy for collinear antiferromagnetic ordering is given by the equation

$$E_{ek}^{col} = \frac{3(3\pi^2)^{2/3} ts}{5\sqrt{2S+1}a^3} \left\{ l \left[\left(n_0 + \frac{\epsilon F}{4\pi el}\right)^{5/3} + \left(n_0 - \frac{\epsilon F}{4\pi el}\right)^{5/3} \right] + 2(L - l)n_0^{5/3} \right\} \tag{43}$$

where s is the surface area. This energy corresponds to the term K_0 in equation (15) (the energy of the d–d exchange is a constant and for this reason is omitted).

One can find the energy E_M corresponding to terms of higher orders in M in equation (15). One should take into account the fact that the magnetization can be non-zero only in the range $[L - l, L]$. Subsequent results will be written in the leading approximation in $\epsilon F/4\pi eln_0$. According to equation (15), for ν close to the boundary density ν_A, equation (16), the magnetization M related to it depends on the density in the following manner:

$$M^2 = \frac{3^{1/3}\pi^{8/3}}{72}(2S + 1)\nu_0^{1/3}(\nu - \nu_A)\Theta(\nu - \nu_A) \tag{44}$$

where $\Theta(x)$ is the Heaviside function, and $\nu_0 = n_0a^3$. Hence, the reduction of the total energy due to canting is

$$E_M = -\frac{K_2^2 ls}{4K_4\nu_A} = -\frac{(3\pi^2)^{2/3}t(\nu - \nu_A)^2 ls}{144(2S + 1)^{1/2}\nu_0^{1/3}\nu_A}. \tag{45}$$

The electric potential ϕ obeys the Poisson equation, coinciding in its form with equation (24). Using it, one obtains the electrostatic energy of the system:

$$E_C = -\frac{\epsilon F^2 ls}{12\pi}. \tag{46}$$

The variational parameter l is to be found from the condition for the minimal total energy $E_{ek}^{col} + E_M + E_C$. At relatively small fields one obtains for l a value close enough to the screening length:

$$l = \frac{\sqrt{3a_B n_0^{-1/3}}}{2} \qquad a_B = \frac{2\epsilon ta^2}{e^2\sqrt{2S+1}}. \tag{47}$$

Then, as follows from equations (41) and (47), the magnetization should appear at the field strength

$$F_A = \frac{4\pi el(n_A - n_0)}{\epsilon}. \tag{48}$$

As seen from equations (44) and (48), the magnetization should depend on the field according to the square-root-like relation:

$$M^2 = \frac{3^{1/3}\pi^{5/3}(2S+1)\nu_0^{1/3}(F - F_A)}{288el}\Theta(F - F_A). \tag{49}$$

One may expect the effect to be considerable both in the rare-earth compounds with $W \gg AS$ (Eu chalcogenides and so on) and in the double-exchange systems with $W \ll AS$ (lanthanum manganites and so on). To confirm this, numerical evaluation of the surface magnetoelectric effect will be carried out. First, the antimagnetoelectric effect in the ferromagnets will be evaluated. With this aim, one should evaluate the ratio of the field-induced and zero-field temperature demagnetizations, i.e., the ratio of the second term in equation (40) for $\langle M \rangle$ and the second term in equation (40a) for M_0, which for $W \gg AS$ is

$$r_{AME} \sim 10^{-2}\frac{(\epsilon eFaAS)^2(\kappa a)}{(e^2/a)^2 T_C^2}\frac{a}{L}. \tag{50}$$

To evaluate the order of magnitude for the antimagnetoelectric effect, equation (50), values of the parameters typical of Eu chalcogenides will be taken. At $\epsilon = 10$, $AS = 0.5$ eV, $T_C = 0.01$ eV, $eFa = 0.3$ eV, $L = 10a$, and $1/\kappa = 3a$, this ratio amounts to 50%, i.e., is quite large. Certainly, the applied field is assumed to be very high, but recent successes in the experimental techniques based on the use of substrates with extremely high dielectric constants make such fields accessible [16].

Using (48) for the double-exchange system, one can also evaluate the field at which the magnetization can appear. If one takes $n_A - n_0 = 10^{20}$ cm^{-3}, $a = 3 \times 10^{-8}$ cm, $\epsilon = 10$, and $l = 3a$, one finds for the field F_A a value of 3×10^5 V cm^{-1}. This field becomes very small at n_0, tending to n_A.

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