Magnetoelectric effects in conductors with mirror isomer symmetry
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INTRODUCTION
As a phenomenon associated with thermodynamic equilibrium, the magnetoelectric effect is observed in magnetic dielectrics which satisfy certain symmetry requirements. By contrast, the kinetic magnetoelectric effect can also occur in nonmagnetic conductors which lack a center of symmetry: in this case the current flow is associated with a magnetization \( M = -\alpha E \), where \( E \) is the electric field. Since the pseudotensor \( \alpha \) contains the relaxation time, it is not constrained to be covariant under time reversal (as it is in other time-dependent phenomena). The magnetoelectric effect appears in its simplest form for conductors with mirror isomer symmetry. In this case, \( \alpha \) has a nonzero trace and reduces to a pseudoscalar for cubic crystals or isotropic stereoisomeric materials; the magnetization \( M \) is thus a multiple of \( E \),

\[ M = \alpha E, \quad (1) \]

where \( \alpha \) has opposite signs for the two different isomers. This is the situation which we consider here. We note that although the magnitude of the magnetoelectric effect may be comparable for arbitrary conductors which have mirror isomer symmetry but lack inversion centers, it diminishes after \( M \) is averaged over the orientation of the crystal axes relative to \( E \). Therefore, there is no magnetoelectric effect in polycrystalline samples.

If the ac field varies slowly enough so that \( M \) and \( E \) are locally related, the Onsager principle and the expression

\[ \delta = \frac{\partial}{\partial t} (\alpha E \cdot MB) \quad (2) \]

for the rate of change in the entropy imply that in addition to containing an ohmic component, the conduction current density \( j \) should also contain a component proportional to \( B \):

\[ j = -\alpha E - \beta B, \quad (3) \]

where \( B \) is the magnetic induction. The total current density also contains the magnetization current \( cV \times (\alpha E) \), so that the volume current density associated with \( B \) is equal to

\[ j = -2\alpha E + cV \times (\alpha E), \quad (4) \]

By virtue of the Maxwell equation \( \nabla \times E = -\frac{\partial B}{\partial t} \), we can regard this contribution to the current as reflecting the fact that under these symmetry conditions, the spatial dispersion \( \epsilon(k) \) contains a term which depends linearly on the wave vector \( k \). We thus have the preliminary order-of-magnitude estimate

\[ \alpha = \text{const} \cdot \langle \alpha E \rangle \quad (5) \]

for \( \alpha \). Here \( \langle \alpha E \rangle \) depends on the diameter of the electrons, and the numerical factor depends on the degree of asymmetry, which is responsible for the \( k \)-linear term in \( \alpha(k) \). Since \( k/e \ll 1 \) for the low frequencies of interest, the effect is small—the current component along \( B \) induced by the ac field in the skin layer is \( 1/\sigma_{\text{mm}} \) times smaller than the component along \( E \). On the other hand, if we compare (1) with the magnetization which is induced by the magnetic field of the current and depends on the diameter \( d \) of the conductor, we find that (1) is dominant for \( d \) up to \( \sim \chi^{-1} \), where \( \chi \) is the magnetic susceptibility of the material.

CONTRIBUTION TO THE ORBITAL MOMENTUM
Both orbital and spin effects can contribute to the magnetization, and we will consider them by using the model employed previously in Ref. 4 to analyze the photovoltaic effect. In this model the electrons are scattered by impurities whose potential lacks an inversion center. We will assume in addition that most of the impurity is in one of the two possible stereoisomeric configurations. In terms of the orientation of the scattering centers, two extreme cases can occur. 1) If both the orientations and the spatial distribution are random then we have a model for an isotropic stereoisomeric medium. 2) If the scattering centers have the same orientation, an anisotropy persists which is dependent on the symmetry of the centers. This case corresponds to a conducting isomer with a plane of mirror symmetry in a simplified model, according to which the potential of the impurities acquires a stereoisomeric distortion induced by the lattice. For cubic symmetry (we will assume this case for simplicity), this implies that the expansion of the impurity potential \( U(r) \) in spherical harmonics must contain at least the two following polynomials:

\[ U(r) = \sum_{l=0}^{\infty} \sum_{m=-l}^{l} \frac{1}{r^{l+1}} Y_{lm}(\theta, \phi), \]

where \( Y_{lm} \) are spherical harmonics.
\[ U_i(r) = \varepsilon g_n(r), \]

\[ U_i(r) = \left[ x^4(y^2z^2) + y^4(z^2x^2) + z^4(x^2y^2) \right] n_i(r). \]  

We first consider the second case; here it suffices that the orientations be correlated over the mean free path \( l \).

Since we want to calculate the coefficient of \( B \) in the current density, by the above discussion we must find the k-linear component of the conductivity tensor:

\[ j_k(k) = \langle B_k \rangle k. \]

where \( \sigma_{\mu\nu} \) is the tensor. The tensor \( \sigma_{\mu\nu} / \partial k_{\mu} \) is completely antisymmetric for a material with cubic symmetry. Writing \( -2 \pi \) for the desired coefficient [as in (4)], we therefore find that

\[ \alpha = \frac{\pi}{\mu} \alpha_{\mu}(0) \partial \sigma_{\mu}(0) / \partial k_{\mu}. \]  

The current density \( j_\mu = Q_{\mu\nu} A_{\nu} \), linear in the electromagnetic field given as usual by a sum of diagrams of the type shown in Fig. 1. The following expression for diagram \( c \) in Fig. 1 illustrates the rule for writing down the time-varying component \( Q_{\mu\nu} \), which determines the conductivity:

\[ \Gamma(p') = \Gamma(p') + \Gamma(p', p) \Gamma(p, p') + \Gamma(p, p') \Gamma(p'), \]  

\[ \sigma_{\mu\nu}(p, e) = \frac{G(p, e)}{G(p, e)}, \]  

\[ G(p, e) = (1 - e - i/2 t)^{-1}, \]  

\[ \sigma_{\mu\nu}(p, e) = \frac{G(p, e)}{G(p, e)}. \]  

Here \( n_i \) is the impurity concentration, \( \varepsilon \) is the electron energy relative to the Fermi level, \( p \cdot k / 2 \), and the relaxation time \( \tau \) is determined by the scattering by the impurities; we omit the Planck constant in the intermediate formulas. Expression (9) contains the scattering amplitudes \( \Gamma(p, p') = \left[ \Gamma(p, p') \right]^{I}, \) which in general must be found to higher order than the Born approximation:

\[ \Gamma(p' \mid p) = \Gamma(p' \mid p) + \frac{d^p}{(2\pi)^4} U_{p' \rightarrow p} G(p') U_{p' \rightarrow p} + \ldots. \]  

We assume in the following estimates that the electron density is typical for a metal and that there are relatively few impurities; \( p \sim 1 \), where \( p \) is the Fermi momentum. In this case most of the contribution to the k-dependence comes from the sections of the diagrams which contain \( g = G^{R} G^{A} \).

If we integrate these sections over \( s \) by the usual change of variable

\[ d^p = m \bar{p} d\bar{p} d\bar{p}', \]

d and defer the angular averaging until later, we find that

\[ \int d^3 g = 2 n \pi \left( 1 - \left( \frac{1}{2} \right)^m + \ldots \right). \]

The expansion parameter here is \( k \). By contrast, the k-dependence of the amplitudes \( \Gamma \) is weak—\( k \) appears only in the Green functions for the intermediate states, and the dependence is determined by the momenta in the region of integration far from the Fermi surface. The expansion here is therefore, in terms of the parameter \( k / p \).

According to (7), allowance for the k-dependence in the central section of diagram \( c \) in Fig. 1 will give a nonzero contribution to \( a \) which is equal to

\[ \alpha = \text{const} \frac{e^2}{h^2} (p/p')^2, \]  

(9)

where \( \text{const} = \frac{1}{12 \pi^2} n_m \left[ \frac{m_i}{\pi} \right] \int d\Omega d\Omega' d\Omega'' \frac{\text{Im} \mathcal{G}(p') \mathcal{G}(p') \mathcal{G}(p') \mathcal{G}(p')}{p_i^4} \) \( [\Gamma(p, p') \Gamma(p', p) \Gamma(p') \Gamma(p')]^{I} \). Because the tensor in (7) is antisymmetric, all three of the independent momenta must appear and it is therefore unnecessary to allow for the k-dependence in the remaining sections of the diagram. For the same reason, diagram \( c \) is the simplest one giving a nonzero contribution to \( a \), and we will confine our analysis to it because the more complicated diagrams do not alter the form of the estimate.

If we recall that

\[ \frac{1}{\tau} = n_i \frac{m_i}{\pi} \frac{d\Omega}{4\pi} \frac{d\Omega'}{4\pi} \frac{d\Omega''}{4\pi}, \]

we see that the constant in (9) depends only on the angular structure of the potential. This is confirmed by the estimate (5), which was derived by qualitative arguments. We note that the Fourier components of the odd-order harmonics of the potential (6) are imaginary (in particular, this is true of \( U_1 \)). The term \( \Gamma^I \) in the second and higher Born approximations therefore contains a component which is odd in the momenta; first order in \( U_1 \), \( \Gamma^I = \Gamma^R + U_1 \), and this component is equal to \( -2 U_1 \text{ Im} \Gamma^R \). The even harmonic \( U_2 \) cancels the antisymmetry of the term \( p g' p' \) with respect to permutations of \( x, y, z \). As a consequence, the angular averaging in (9) gives a nonzero result.

We now briefly analyze what happens when the scattering centers are randomly oriented. In this case the harmonics (6) must be expressed in an arbitrary reference frame, and the final result must be averaged over the frame orientations independently for each center. It is easy to see that the contribution from the k-dependence in the g sections now vanishes (this contribution was large in the previous case). In-
deed, if we average $F^J(p_1, \ldots, p_n)$ over the frame orientations, the result must be a pseudoscalar combination of the external momenta; the only combination with these properties is of the form $k \cdot p_1 \cdot \ldots \cdot p_n$. We must therefore allow for the dependence of $F$ on $k$, as a result, the magnitude of the magnetoelectric effect in this case turns out to be $1/p_d$ times the magnitude for (5).

If the current and electric field distributions are uniform, we can immediately calculate the magnetic moment associated with the orbital momentum. We immediately obtain the result (7) for $M = \alpha E$ from the definition

$$[M] = \frac{1}{2} \int dV(r)$$

of the moment. The coefficient of $E$ in the expression for the magnetic moment is thus $-1/2$ times the coefficient of $B$ is the expression for the current.

We have preferred to start with the expression for the current, because this enables us to treat the case of strong spatial dispersion directly. As we noted in the Introduction, the conjugate current reaches a maximum for $kl \sim 1$, i.e., for $l \sim \Delta_{\text{sw}}$. This effect is analogous to the rotation of the polarization plane in optics; however, the concept of orbital magnetization becomes meaningless for $kl \sim 1$.

**SPIN POLARIZATION INDUCED BY THE ELECTRIC FIELD**

As in the previous section, we will find the current $-B$ associated with the interaction between the spin and the magnetic field. Of course, this current is due entirely to the spin-orbit interaction, and the interaction of the spin with the impurity potential is decisive here. By contrast, the direct effects of the electric field on the spin are much weaker and do not cause longitudinal polarization.

The physical picture is as follows. The nonequilibrium component of the spin fluctuation (which is determined by the rate of change $B$ of the magnetic field) induces a current fluctuation via the spin-orbit interaction with the stereoisometric impurity. Since the spin fluctuation amplitude is proportional to the spin relaxation time for low frequencies, the current is not multiplied by the relativistically small factors associated with the spin-orbit interaction.

Figure 2 shows a diagram for the relevant contribution to the current: it corresponds to the expression

$$J_n = \frac{e}{2mc} \frac{n_1}{2} \int_0^1 \xi_0 \xi_1 \cdots \xi_n \left\{ \partial x \Delta \xi \right\} \left( -ie \Delta \xi \right).$$

(10)

Here we have already carried out the integration over $\xi$, which leads as in (8) to the factor $a_0$. We have also integrated over $p$ in the right-hand section of the diagram. The hatched region denoted by the symbol $\Delta_\sigma$ contains the spin-orbit interaction and takes the current vertex into a spin vertex. We will find its structure in more detail below. The wavy line corresponds to the operator $D(k, \omega)$, which acts on the spin and is given by the usual sum of ladder diagrams. We introduce the notation

$$f/2 \begin{array}{c} \tau \cr \omega \cr \sigma \cr \partial \end{array} \partial 

\begin{array}{c} D \cr \Delta \cr \xi \cr \sigma \cr \tau \cr \partial \end{array} \partial + \frac{\xi^2}{\Delta \tau} \partial

D_\sigma = \left( -i\omega \Delta + \partial \right)^{-1} \partial a_0,$$

(11)

for the trace. If we include only the isotropic part of the impurity potential and the corresponding component of the spin-orbit interaction in the calculation of $D$, we get

$$D_\sigma = \left( -i\omega \Delta + \partial \right)^{-1} \partial a_0,$$

(11)

where $D = p_d/3m$ is the diffusion coefficient, and the reciprocal spin relaxation time $\tau_{\text{sw}}$ is second-order in the small spin-orbit interaction constant $A = \frac{2e}{\hbar k}$. A more detailed examination shows that under our symmetry conditions, $\left( D^{-1}\right)_{\mu \nu}$ contains a linear term proportional to $\epsilon_{\mu \nu} \xi_k$ which causes the spin to rotate during the diffusion process.

We will discuss the additional features of the spatial dispersion elsewhere; here we confine ourselves to the region $\omega \tau_{\text{sw}} < 1$, $D/\tau_{\text{sw}} \ll 1$ for which the dispersion $\theta(k)$ can be neglected.

Assume that a magnetic field $B_0$ has been turned on; we then find the expression

$$D^{-1} = \left( 2n_1 \partial_\mu \partial_\nu B_0 + \partial_\mu \partial_\nu \right),$$

(10)

for $D^{-1}$ which allows for the spin precession (here $\mu_0 = e/2mc$). If $B_0 = (0, 0, B_0)$, the nonvanishing components of $D_{\mu \nu}$ are equal to

$$D_{x x} = D_{y y} = D_{z z} = -\frac{\omega \tau}{1 + (\omega \tau)^2} \partial \xi_0 \xi_1,$$

$$D_{x y} = D_{y x} = D_{x z} = D_{y z} = D_{z y} = D_{z x} = -\frac{\omega \tau}{1 + (\omega \tau)^2} \partial \xi_0 \xi_1,$$

$$D_{x \nu} = D_{\nu x} = D_{y \nu} = D_{\nu y} = D_{z \nu} = D_{\nu z} = -\frac{\omega \tau}{1 + (\omega \tau)^2} \partial \xi_0 \xi_1,$$

(12)

where $D_\sigma = D_{\mu \nu}$.

We now discuss the structure of $D_\sigma$ in (10). Unlike the orbital mechanism, which was determined by the $k$-linear term in the nuclear dispersion and was therefore very sensitive to the degree of correlation of the impurity orientations, the spin-associated effect does not depend significantly on the correlation. In our estimate we therefore need consider only the interaction with a single impurity. Figure 3 shows a typical diagram for $D_\sigma$ to fourth order in the impurity potential. Additional diagrams with different configurations of the impurity vertices on the electron lines must also be considered. It is readily shown that the effect of interest first appears in fourth-order perturbation theory. In fact, the contribution to the coefficient $a$ for a single center must be independent of the orientation of the center. We can therefore average over the orientations of the frame in terms of

![FIG. 2](Image)

![FIG. 3](Image)
which the asymmetric part of the potential is expressed. Only the product $\Pi U(q_i)$ of the amplitudes is averaged in the expression corresponding to the diagram; this product must change sign if all the $q_i$ are replaced by $-q_i$. The averaged expression will contain an invariant factor of the form $q_i \cdot q_j$. However, since $\sum q_i = 0$ in the diagram, the diagram must contain at least four amplitudes.

The next step is to integrate over the momenta $p_i$, $i = 1, \ldots, 4$; the differences between these momenta also appear in the amplitudes $U(q_i)$. It is important to note that we may neglect the dependence on the momenta in the diffusion ladder included to the right of the portion of the diagram corresponding to $\delta_{\mu \nu}$, because this dependence occurs only in the angular harmonics for which the denominator in (11) is not small. Since $\sigma_{\alpha \nu}$ is the only vector which can result from the integration, we must have

$$\delta_{\alpha \nu} = \sigma_{\alpha \nu}. \tag{13}$$

The spin operator appears because of the spin-orbit interaction, which contains the term $\sigma \cdot p \times p'$ and the constant $A$ defined after Eq. (11) above. We easily see that to first order in $A$, the entire expression reduces to an integral of a derivative with respect to the momentum and therefore vanishes. This is not true to second order in $A$, because the spin matrices do not compute. The same conclusion of course also holds for the more complicated diagrams. The expression

$$a' = A^4 \int \frac{d^3p_i}{(2\pi)^3} \int \frac{d^3p_j}{(2\pi)^3} \left\{ 2 \cdot \frac{p_i \cdot p_j}{16\pi^4} \right\} \left\{ \left( \frac{p_i \cdot p_j}{16\pi^4} - \frac{1}{16\pi^4} \right) \right\} \delta_{\alpha \nu} \delta_{\beta \mu} \delta_{\gamma \lambda}, \tag{14}$$

can be derived after some manipulation. Here $dp$ is the complete phase volume element for the momenta $p_i$, where $\xi$ appears in the denominators, the integrals must be regarded as principal value integrals. The form of the potential must be specified in order to proceed further in the calculations. We will therefore confine ourselves to the rough estimate

$$a = A^4 m(p_i), \tag{15}$$

which will also be needed in the next section.

As usual, the total current density, including the interaction of the spin with the magnetic field, also contains a term $c' \mathbf{V} \mathbf{M}$. However, the diagram giving the part of $c' \mathbf{M}$ proportional to $E$ is clearly the same as the one in Fig. 2, except that the current and spin vertices are interchanged. In the absence of a constant magnetic field, we thus again find that

$$1 = -2\pi B, \quad M = a_e E$$

and $a_e \sim (\hbar/\epsilon)(\epsilon_p)$ as in the case of the magnetoelectric effect associated with the orbital interaction for randomly oriented impurity centers.

We see from (12) that if $B_x = 0$ then $J$ and $M$ contain components proportional to $B_x \times B$ and $B_x \times E$, respectively. The entire spin current is suppressed in a transverse field if $\tau_x \epsilon x > 1$.

The relevant diagram is shown in Fig. 4, where both of the current vertices have a structure $\delta_{\mu \nu}$ of the type (13). If we use the expressions for $D$ (the wavy line in the diagram), we immediately get

$$\delta_{\alpha \nu} = \delta_{\alpha \nu} - \sigma_{\alpha \nu} A^4 \frac{1}{1 + (a_x)^2}, \quad \delta_{\alpha \nu} = \sigma_{\alpha \nu} A^4 \frac{\omega_x}{1 + (a_x)^2}.$$

for the corrections to the components $\sigma_{\alpha \nu}$ in a magnetic field along the $z$ axis. The numerical constant depends on the form of the scattering potential. We see that even though the positive correction to the transverse conductivity is extremely small, its contribution to the magnetoresistance for fields $a_x \epsilon_x - a_x \epsilon_y A^4 \epsilon_x > 1$ is larger than the usual contribution by a factor of $A^{-2}$. For this range of fields, the contribution to the Hall effect is also large and essentially determines the nature of the nonlinearity.

CONCLUSIONS

The above estimates are physically quite transparent and predict effects which should be experimentally accessible. The chief obstacle to observing these effects is the exotic nature of the materials which exhibit them. Materials with the metallic conduction and symmetry required are probably not available at the present time. Semiconductors show greater promise in this regard, but in this case the estimates apply only in a rough, qualitative form. It is worth noting here that magnetoelectric effects of comparable magnitude but with a more complicated tensorial structure should also occur in arbitrary conductors which lack inversion centers. As we mentioned in the Introduction, the principal difference is that the tensor does not reduce to a pseudoscalar for conductors without a plane of mirror symmetry; single crystals will therefore be needed to observe the magnetoelectric effect. We also note that any crystal lacking an inversion center can be turned into a stereoisomer by uniaxially compressing it along an arbitrary direction (with the exception of certain symmetry axes). Of course, the characteristic iso-

![FIG. 4](image-url)
meric effects will be small in this case unless the lattice distortion is large.

The above analysis has several qualitative consequences, one of which is that the spin fluctuations participate directly in electron transport phenomena for materials with mirror isomer symmetry. For a ferromagnetic material, the naive self-consistent field theory predicts that the exchange interaction will increase the coefficient α without limit as the Curie point is approached. We therefore expect that the magnetic transition in this case will also be accompanied by important changes in the electrical properties of the conductor.

We thank L. P. Gor'kii, V. N. Gribov, and E. E. Khmel'nitskii for a discussion of some of the problems considered above.


Translated by A. Mason