Magnetoelectric effect in mixed-valency oxides mediated by charge carriers

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Abstract – We show that the presence of free carriers in a substance can generate the multiferroic behavior. Namely, if the substance has mixed-valence ions, which can supply free carriers and have electric dipole and spin moments, all three types of long-range order (ferromagnetic, ferroelectric and magnetoelectric (ME)) can occur at low temperature. The physical origin of the effect is that charge carriers can mediate the multiferroic behavior via spin-spin (RKKY), dipole-dipole and dipole-spin interactions. Our estimate of the interaction magnitude shows that there exists an optimal carrier concentration, at which the strength of ME interaction is maximal and comparable to that of spin-spin RKKY interaction. This permits to conclude that in substances, where RKKY interaction between local spins is not small, a substantial value of free-carriers–mediated ME interaction can occur. Our analysis shows that disorder in the above substances does not suppress multiferroic effects.

Multiferroics are substances which can simultaneously exhibit spontaneous polarization, magnetization and/or strain \cite{1}. The ferroics where magnetic and electric orders coexist have recently become the focus of intensive research \cite{2–4}, magnetism and ferroelectricity being involved with local spins and off-center structural distortions (electric dipoles), respectively. The physical nature of the coexistence of these two seemingly unrelated phenomena as well as of the recently observed \cite{3} strong interaction between polarization and magnetization (magnetoelectric (ME) coupling) is not completely understood up to now, because trivial spin-orbit interaction can be the source of a very small ME effect only. The clarification of the physical nature of the above phenomena would be of great importance both for fundamental research and for the creation of a new generation of electronic devices. In particular, the ME effect in multiferroics opens the way to write an information with the help of the electric field and to read it with the help of the magnetic field making the memory devices more stable and reliable \cite{5}. Among different multiferroics with high ME effect the oxides seem to be the largest group. Namely, perovskite rare-earth manganites $\text{RMnO}_3$ ($\text{R}=\text{Eu, Gd, Tb and Dy}$) \cite{3,6}, perovskite-type $\text{BiFeO}_3$, $\text{BiMnO}_3$ (see ref. \cite{7} and references therein), materials with general formulae $\text{R Mn}_2\text{O}_5$ ($\text{R}=\text{Tb, Y, Eu}$) \cite{2,4} and other oxides belong to this group \cite{1}. It is easy to see that one of these oxides cations belongs to the ions of $3d$-group known to have several valency states. Such ions are $\text{Mn}^{2+}$, $\text{Mn}^{3+}$, $\text{Mn}^{4+}$, $\text{Fe}^{2+}$, $\text{Fe}^{3+}$, $\text{Cr}^{3+}$, $\text{Cr}^{5+}$ etc. The presence of these ions has been observed by ESR and optical methods \cite{8} so that mixed valency is expected to occur in the above materials. Moreover, due to the chemical and structural complexity of $\text{RMn}_2\text{O}_5$, $\text{Mn}^{4+}$ ions are octahedrally coordinated by oxygen, whereas $\text{Mn}^{3+}$ are at the base center of a square pyramid \cite{2} so that the general formula of this oxide can be rewritten as $\text{R}(\text{Mn}^{4+}\text{Mn}^{3+})\text{O}_5$ with equal number of $\text{Mn}^{4+}$ and $\text{Mn}^{3+}$. So, the cation valency depends on the local symmetry, defined by the number of surrounding oxygen ions. However it is known that the

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oxides used to have a lot of oxygen vacancies (and possibly other imperfections) randomly distributed in the host lattice. This can lead to a random distribution of cations with different valency, some of them can be magnetic or nonmagnetic (if their ground-state spin is zero). On the other hand, oxygen vacancies can generate free carriers so that the afore-mentioned oxides can acquire nonzero conductivity equal to that of semiconductors. It had been shown [15] that in diluted magnetic semiconductors (DMS) (for instance Ga\(_1-x\)Mn\(_x\)As), also belonging to the above class of mixed-valency substances, ferromagnetism appears due to Ruderman-Kittel-Kasuya-Yosida (RKKY) indirect coupling between Mn \(d\)-shell localized magnetic moments mediated by the induced spin-polarization in a free-hole itinerant-carrier system. The experimental investigation of (Ga, Mn)As DNS [16] shows that the temperature of the ferromagnetic phase transition is \(T_c = 110\) K or even \(T_c = 173\) K [17], which is quite a large value allowing for the randomness of the Mn ions distribution. Since it is not excluded, that the ion (for example off-center Mn) can have both spin and electric dipole moment, the above substances could be the “candidates” for realization of all three types of long-range order — ferromagnetic (due to RKKY interaction), ferroelectric (due to carrier mediated dipole-dipole interaction, see, e.g., ref. [18]) and ME order, also carrier-mediated. This means that the interaction via charge carriers can make the above substance a multiferroic. Note, that phases with ME order belong to secondary ferroics with order parameter involving both magnetization and polarization [19], their domain state can be switched by simultaneous application of magnetic and electric fields [20].

If local spins and electric dipoles (off-center ions) are randomly distributed over the host lattice sites, the overall thermodynamic behavior depends on the history of the sample i.e. heating and/or cooling. These effects, characteristic for disordered systems [21], have been observed in ferroics with a high ME effect [2].

In the present paper we show that the microscopic nature of the magnetoelectric (ME) effect might be the interaction between local spins and dipoles via free charge carriers in a mixed valence oxide. In other words, if the substance under consideration has free carriers, they can mediate the ME effect. In the mean-field approximation, we calculated for the first time the magnitude of carrier-mediated ME interaction and compared it to both the conventional RKKY interaction and the dipole-dipole one. We obtain that the ME interaction oscillates with the ratio \(k_Fd\) (\(k_F\) is the Fermi wave vector, \(d\) is the off-center ion displacement) and find the optimal value of \(k_F\) (and hence the free-electrons concentration \(n_e\)) when the ME interaction magnitude is the same as that of the RKKY interaction. The dipole-dipole interaction magnitude is always smaller than both RKKY and ME. This permits to hope that in the substances, where the RKKY interaction between local spins is not small, one can also achieve a substantial value of the ME interaction along with the multiferroic state.

The global symmetry of the linear ME effect implies the simultaneous breaking of time-reversal and inversion (say “space-reversal”) symmetries of a substance. To break both the above symmetries simultaneously, one needs to have in a system both spin moments \(\vec{S}\) (axial vectors, changing their directions at time reversal) and dipole moments \(\vec{d}\) (in other words, two-level system (TLS), see, e.g. [18]), changing their directions at spatial coordinates direction reversal. For a microscopic description this means that a system Hamiltonian should incorporate the “usual” terms proportional to \(\sum_{ij} J_{SS}(\vec{r}_{ij})\vec{S}_i\vec{S}_j\) and \(\sum_{ij} J_{dd}(\vec{r}_{ij})\vec{d}_i\vec{d}_j\) (responsible for magnetic and electric long-range order, respectively) as well as coupling terms proportional to \(\sum_{ij} J_{sd}(\vec{r}_{ij})\vec{S}_i\vec{d}_j\). In our model, the latter term is responsible for the ME effect in a solid.

To account for the above effect microscopically, we should find explicitly the potentials of interaction \(J_{AB}\) (A, B = S, d). The ubiquitous method of calculation of the above interaction potentials \(J_{AB}\) is the perturbation theory. In this approach, we have two “zeroth” Hamiltonians — free electrons, TLSs, or spins. The interaction term
might be dipole-dipole (dd), spin-spin (SS) or dipole-spin (SD) interaction. If this term is considered to be small, we can apply the perturbation theory and get the interaction potential, as usual, in its second order. The details of calculations of dd and SS interactions can be found in refs. [18,22] and [23,24], respectively. Our aim is to calculate the SD interaction. This will be done similarly to the above interactions, using the second-order correction to the ground-state energy \( E^{(2)}_{AB} (A,B=S,d) \). This expression reads [23]

\[
E^{(2)}_{AB} = \sum_{ik} J_{AB}(r_{ik}) A_i B_k,
\]

where for finite temperatures

\[
J(r) = \sum_{k_1 \neq k_2} \frac{|U(k_1 - k_2)|^2 n_{k_1} (1 - n_{k_2})}{\xi_{k_1} - \xi_{k_2}} \times \exp[\text{i}(k_1 - k_2)r], \quad n_k = \frac{1}{\exp\left(\frac{\xi_k - \mu}{T}\right) + 1}.
\]

Here \( U(k_1 - k_2) \) is the corresponding interaction amplitude, \( \mu \) is the chemical potential. Actually, the specific form of \( J(r) \) (i.e. dd, SS or SD) depends on the form of \( U(k_1 - k_2) \). Here \( \xi(k) \) is a dispersion law for free electrons

\[
\xi(k) = \frac{k^2}{2\mu}, \quad (3)
\]

and \( n_k \) are Fermi-Dirac factors.

Although the finite temperature effects might be important, it can be shown that all important physics comes from the zero-temperature case. This means that we may safely use the zero-temperature approximation, which is actually used, for example, in the RKKY interaction derivation [24]. At zero temperature the occupation numbers are simply unit step functions \( \theta(\xi(k) - E_F) \), where \( \mu(T = 0) = E_F \) is the Fermi energy.

The coupling function \( U(k_1 - k_2) \) is expressed via the expansion over spherical harmonics of the angle \( \theta_{k_1,k_2} \) between vectors \( k_1 \) and \( k_2 \), see ref. [18] for details. It can be shown that for our purposes it is sufficient to consider the function \( U \) to be isotropic, i.e. to use the zeroth term of this expansion

\[
U(k_1 - k_2) \equiv a_0 \phi(k_1 - k_2), \quad (4)
\]

and the function \( \phi(k_1 - k_2) \) actually determines the kind of interaction (SS, dd or SD).

The spin-spin term \( J_{SS} \) is indeed a well-known RKKY interaction, in this case \( \phi_{SS}(k_1 - k_2) \equiv \phi \) and

\[
J_{SS}(r) = \frac{mV^2a_0^2k_F^4}{2\pi^2\hbar^2} \sin x - x \cos x \frac{1}{x^4}, \quad x \equiv 2k_F r, \quad (5)
\]

where \( V \) is the crystal volume.

For the calculation of dipole-dipole coupling the interaction function should be chosen in the form [18]

\[
\phi_{dd}(k_1 - k_2) = \text{i} \sin \left( \frac{1}{2} |\text{d}(k_1 - k_2)| \right).
\]

Substitution of this function into eq. (2) at zero temperature after a straightforward but lengthy calculations yields

\[
J_{dd}(r) = -\frac{mV^2a_0^2k_F^4}{8\pi^2\hbar^2} \left[2F(x) - F(\psi_+) - F(\psi_-)\right],
\]

\[
F(y) = \frac{\sin y - y \cos y}{y^4}, \quad x = 2k_F r, \quad \psi = a_x \pm \frac{d}{r}, \quad d \equiv |\text{d}|,
\]

\[
\alpha \text{ is the angle characterizing the direction of vector d (for example, it can be thought as the angle between d and the z-axis). It is well known (see above) that the off-center ions can have several orientations in a host lattice. The different orientations mean different values of the angle } \alpha. \text{ For example, for a two-position orientable dipole } \alpha = 0, \pi. \text{ This fact will be used below.}
\]

The SD interaction potential will also depend on the angle \( \alpha \), its function \( |U(k_1 - k_2)|^2 = a_0^2(\phi_{SS}^2 + c.c.) \) (c.c. stands for complex conjugated). This yields

\[
J_{sd}(r) = -\frac{ma_0^2V^2k_F^4}{4\pi^2\hbar^2} \left[F(\eta_-) - F(\eta_+)\right],
\]

\[
\eta_{\pm} = b_{\pm} x, \quad b_{\pm} = \sqrt{1 + \frac{1}{4} \alpha^2 - \lambda \cos \alpha},
\]

Expression (7) gives the desired potential of spin-dipole interaction mediated by charge carriers.

To estimate the magnitude of the ME interaction, we calculate Weiss mean fields, related to SS, Sd and dd interactions. Having the interaction \( J_{AB}(r) \) (A,B = S,d), the Weiss field is defined as

\[
W_{AB} = \frac{1}{V} \int_V J_{AB}(r) d^3 r,
\]

where \( V \) is the crystal volume. Since all \( J_{AB}(r) \) except RKKY (5) depend on \( d \) — the ion off-central shift, the resulting integrals will be oscillating functions of this parameter (to be more specific, the parameter is \( k_F d \)). This means that depending on the \( k_F d \) value, the corresponding Weiss fields may be positive or negative, defining the mutual direction of spins and dipoles in ferroelectric and magnetoelectric phases.

We recollect here, that in the mean-field approximation the temperatures of the transition to ferromagnetic, ferroelectric and magnetoelectric phases are related to the corresponding Weiss fields in an obvious fashion: \( T_{AB} = \frac{1}{\eta_{AB}} |W_{AB}| \), where \( n_{AB} \) is the concentration (number of particles per unit volume) of local spins or electric dipoles.

Expressions (6) and (7) show that the corresponding integrals cannot be done analytically. Substitution of the RKKY potential (5) into eq. (8) yields

\[
W_{SS} = \frac{1}{4} W_0, \quad W_0 = \frac{m^2 V a_0^2}{\pi^2 \hbar^2}. \quad (9)
\]
The estimate for $W_0$ here gives $W_0 \approx 500 \text{ K}$ [18]. In that case $W_{SS} \approx 125 \text{ K}$. The results of numerical calculation of $W_{Fd}$ (ME interaction) and $W_{dd}$ (dipole-dipole interaction) are reported in fig. 1 at different angles $\alpha$. It is seen that while the magnitude of the magnetic interaction $W_{SS}$ is constant, the magnitudes of dd and Sd interactions oscillate with the parameter $k_Fd$. Moreover $|W_{dd}| < |W_{Sd}| < W_{SS}$ and at $\alpha = 0$ and $k_Fd \approx 1.4$ the value of $|W_{Sd}|$ is maximal, it is almost equal to $W_{SS} = 0.25W_0$ and is much greater than $|W_{dd}|$. Actually, the ME effect can be realized in a broader interval (see MD curve for $\alpha = 0$ in fig. 1) $|W_{Sd}| > 0.5|W_{Sd}|$ so that $0.5 \leq k_Fd \leq 1.4$. This means that for a substance, having oxygen vacancies (which is a source of free carriers) and ions with off-center shift $d$ there is a strong possibility for substantial ME coupling via free carriers.

We estimate carriers concentration in the above $k_F$ interval with the help of expression $n_e = \sqrt{n_0Tc} \times \exp(-E_F/T)$, valid for low temperatures $T \leq 100 \text{ K}$ [25], where $n_0 \approx (10^{22} - 10^{23}) \text{ cm}^{-3}$ is the high-temperature value of carrier concentration, $n_FV = 10^{17} \text{ cm}^{-3}$ is the oxygen vacancies concentration, $E_F = \hbar^2k_F^2/(2m^*)$ is the Fermi energy and $m^*$ is the carrier effective mass. For $d = 0.5 \cdot 10^{-8} \text{ cm}$, $m^* = 10m_e$, we obtain $n_e \approx (10^{16} - 10^{17}) \text{ cm}^{-3}$, which is a typical value for semiconductors. Having these values, we now discuss the influence of the screening of the electric dipoles by the itinerant charges on the potential of the spin-dipole interaction (7). Such screening would be significant if its characteristic length $l$ is smaller than the radius of interaction (7). It is known (see, e.g., ref. [9]) that $l$ has the order of magnitude of the $180^\circ$ ferroelectric domain wall thickness in a material, while the effective interaction (7) radius can be estimated as $1/k_F$. In terms of the parameter $\gamma = k_Fd$ the above condition of essential screening can be rendered as $\gamma < d/l$. For the above value $d = 0.5 \cdot 10^{-8} \text{ cm}$ and the typical value $l = 10^{-7} \text{ cm}$ [9], we have $k_Fd < 0.05$, which means that almost the entire “phase diagram” in fig. 1 is not affected by the screening. The inclusion of angle $\alpha$ will not change this estimate drastically so that we may safely conclude that in the above physically important range of $k_Fd$ the screening will not play an important role.

If the above substances have other (than oxygen vacancies) sorts of defects, which can supply the free charge carriers, the above interactions are stronger, promoting the multiferroic behavior at low temperatures ($T \leq 100 \text{ K}$). Note, that many single-phase multiferroics exhibit multiferroicity only at low temperatures [2]. Our analysis shows (see refs. [26–28]) that the randomness in the above ion positions as well as the presence of other types of unavoidable technological defects in a substance plays a dual role. On the one hand, it tries to destroy all the three kinds of the above long-range order, the most sensitive ferroelectric one, which is due to dipole-dipole interaction. On the other hand, this disorder might supply extra free electrons or holes, which promote the considered effects. Moreover, the long-range magnetic order (due to RKKY interaction) is least sensitive to disorder and ME order is an intermediate case. Thus we come to the conclusion that disorder in the above substances would not adversely influence the initial ME order.

It is also seen from fig. 1 that since RKKY interaction is dominating in the problem under consideration, the other important factor needed for the ME effect to be realized is a sufficient strength of spin-spin (RKKY) interaction via free carriers. If the $T_c$ related to RKKY interaction is around $150 \text{ K}$, then (see fig. 1) the ME phase transition temperature $T_{c,\text{ME}}$ will be of the same magnitude. Moreover, the maximal value of $T_{c,\text{ME}}$ occurs for $\alpha = 0$, i.e. for a two-site orientable dipole. For other angles $\alpha$ and parameters $k_Fd$ the situation is also not that critical, the only “forbidden” values $k_Fd$ are those where $W_{Sd} = 0$, $\alpha = 90^\circ$ (see fig. 1). This shows that there is a large space of parameter values where the ME effect mediated by free carriers can be realized in the above substances.

To conclude, we have shown that it is quite probable to obtain a sufficiently strong ME coupling mediated by free charge carriers in mixed-valency oxides. Namely, in the substances, where RKKY interaction between local spins is not small, and the free carrier concentration is related to the off-center shift, a substantial ME coupling may be realized. Smaller (but still sensitive) values of the above coupling occur in the entire domain of $k_Fd$ values except those where $W_{Sd} = 0$ (see fig. 1). Our preliminary analysis shows that the effects of disorder influence multiferroic behavior in the above substances but do not suppress it. The results of quantitative consideration of disorder effects leading, for example, to the dependence of ME characteristics on the sample history [29] will be published elsewhere.
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