Vibronic orbital magnetism

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Abstract. It is shown that in systems lacking the time inversion symmetry operation the Jahn-Teller effect could be the reason of the existence of the electronic magnetic moment. In crystals with cooperative Jahn-Teller effect the last could be responsible for the vibronic magnetism – ordering of vibronic magnetic moments. The direct connection between the vibronic magnetism and piezomagnetism is discussed. If the local crystal symmetry is lacking both – the time and space inversion symmetries – the cooperative Jahn-Teller effect leads to the creation of the Jahn-Teller multiferroics.

1. Introduction.
Vibronic orbital magnetism is a complex of phenomena related to the orbital momentum of electrons that becomes important only if the electron-vibrational (vibronic) interaction in the system under discussion is not zero.
In general the magnetic moment of any structural crystal unit or molecule is containing two contributions coupled with electrons and nuclei correspondingly
The magnetic moments in the formulae (2) and (3) are given by

\[ \vec{M}_{el} = -\frac{e}{2mc} \sum_{i} [\vec{r}_i \times \vec{p}_i] \]  

(2)

\[ \vec{M}_{nucl} = \frac{e}{2c} \sum_{i} [\vec{R}_i \times \vec{P}_i] \frac{Z_i}{M_i} \]  

(3)

In the formulae (2) and (3) e is the electronic charge, m – mass of the electron, \( p_i \) is the electronic impulse conjugated to the electronic radius \( r_i \), \( R_i \) and \( P_i \) are the radius and the impulse of a nucleus, \( Z_i \) and \( M_i \) are the effective nucleus charge and mass, \( i \) is the summation index over the structure units or molecules.

Each of the magnetic moments (2) and (3) in general may have a contribution corresponding to the fixed equilibrium positions of the nuclei and a component related to the displacement of the nuclei from equilibrium – vibronic interaction contribution.

In this presentation we will consider the electronic magnetic momentum only and only its part that becomes zero in the absence of vibronic interaction. We do not discuss here any effects and difficulties related to the finite size of crystals or crystal interfaces.

In other words we will consider \( M_{el} \) as

\[ \vec{M}_{el} = -\frac{e}{2c} \sum_{i} \langle \Phi_i | \vec{r} \times \vec{v} | \Phi_j \rangle \neq 0 \]  

(4)

and will analyze at what conditions \( M_{el} \) is not zero due to vibronic interaction, if the wave functions \( \Phi_i \) in (4) are the components of an orbitally degenerate or pseudo degenerate (separated by a relatively small energy gap) electronic state.

In some sense the situation is similar to the vibronic dipole moment concept which was developed by Bersuker in [1] (see the references in [1]). The projections of the orbital momentum \( \vec{L} = \vec{r} \times \vec{p} \) are not zero only in the case of the broken time inversion symmetry. From the first point of view the last statement is closing the problem: only the interactions that are breaking the time inversion symmetry are responsible for the creation of the magnetic moment. However, in the presence of the broken time inversion symmetry the vibronic interactions may create new, initially
absent magnetic moment projections. Going back to the analogy with the vibronic electric dipole moment concept it should be noted that the electric vibronic dipole moment exists in case of orbital degeneracy (not only pseudo degeneracy), if the system is lacking the space inversion center. In this situation the local distortions create an electric dipole moment as a result of Jahn-Teller (not only pseudo Jahn-Teller) effect as it was mentioned by Vekhter in [2]. Similarly to the electric dipole moment the magnetic vibronic moment can exist in case of orbital degeneracy and pseudo degeneracy if the local time inversion center is absent. From the macroscopic (phenomenological) point of view the formation of electric and magnetic dipole moments as a result of a distortion in a system without space and time inversion symmetry correspondingly is a well known phenomenon of piezoelectricity or piezomagnetism. It is completely clear that if the system is lacking both symmetry operations – space inversion and time inversion – the Jahn-Teller distortion creates both the electric and magnetic dipole moments. This together with the electronic structure of the unit (molecule) could be considered as a guide to a search of molecules with both – electrical and magnetic – moments. In case of crystals containing at least one such a unit sublattice the cooperative Jahn-Teller effect could lead to the formation of multiferroic compounds. The idea of interrelation of the crystal distortions and magnetoelectricity is not new. The phenomenology of the striction mediated magnetoelectricity was suggested by Mitsek and Smolensky in [3]. The cooperative Jahn-Teller effect based microscopic theory of magnetoelectricity was considered by Kaplan and Vekhter in [4] and later developed by Kaplan in [5, 6]. However on the contrary to the first publications where the electro- and magnetostriction were in the center of the microscopic mechanism discussion, here the microscopics of piezomagnetism – vibronic magnetism – is under consideration.

2. **Microscopic model.**

Below the application of the suggested in the introduction ideas is illustrated for a following microscopic model. A tetragonal crystal containing a sublattice of ions with the lowest electronic orbital doublet – singlet energy structure is considered. The crystal is magnetically ordered (ferromagnetism is accepted initially for simplicity), the local magnetic moments at T<T_m are parallel to the crystal a-axis (it is accepted that the intersite magnetic interactions for the x- and y-components of the magnetic moments is much bigger than for the z-components).
Among the vibronic interactions the interaction of the electrons with the E-symmetry local distortions and the corresponding monoclinic strains is considered the strongest.

After the standard in the cooperative Jahn-Teller effect theory shift transformation [4] in the second order in vibronic interaction theory of perturbation the electronic part of the crystal Hamiltonian can be presented as

$$\hat{H} = -\Delta \sum \hat{Q}_m - \sum A_{mn} (\hat{P}_{xm} \hat{P}_{xn} + \hat{P}_{ym} \hat{P}_{yn}) - \sum J_{mn} (\hat{S}_{xm} \hat{S}_{xn} + \hat{S}_{ym} \hat{S}_{yn}) -$$

$$- h_x \hat{S}_{xm} - h_z \hat{S}_{zm}$$

(4)

In the Hamiltonian (4) $\Delta$ is the energy gap between the ground electronic doublet and the exited singlet, $A$ and $J$ are constants of the intersite interactions caused by virtual phonon exchange and magnetic dipole-dipole or exchange interactions correspondingly, $h_x$ and $h_z$ are the components of the external magnetic field. For simplicity the small vibronic reduction of the magnetic interactions is ignored. The electronic operators $\hat{Q}$, $\hat{P}$, and $\hat{S}$ on the given electronic basis are described by the following matrices

$$Q = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 0 \end{pmatrix} \quad P_x = \frac{1}{\sqrt{2}} \begin{pmatrix} 0 & 0 & 1 \\ 0 & 0 & -1 \\ 1 & -1 & 0 \end{pmatrix}$$

(5)

$$S_x = \frac{1}{\sqrt{2}} \begin{pmatrix} 0 & 0 & 1 \\ 0 & 0 & 1 \\ 1 & 1 & 0 \end{pmatrix} \quad S_z = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 0 \end{pmatrix}$$

At $T<T_m$ the magnetic phase transition takes place, and $\bar{S}_{xm} = S \neq 0$, $\bar{S}_{ym} = 0$.

At the lower temperature $T=T_s<T_m$ the structural phase transition from the tetragonal to the monoclinic phase takes place, and now $\bar{P}_x = P \neq 0$, $\bar{P}_y = 0$.

The homogeneous monoclinic crystal strain $U_{xz}$ is proportional to the average of the electronic operator $P$

$$U_{xz} \sim \bar{P}.$$
The electronic energy spectrum of the crystal is defined by the following equation

\[ \hat{H}_{mol} = -\Delta \sum_m \hat{Q}_m - AP \sum_m \hat{P}_{xm} - H_x \sum_m \hat{S}_{xm} - h_z \sum_m \hat{S}_{zm} \]  

where

\[ A = \sum_n A_{mn} = \sum_{m\kappa} V_{\kappa}^{x} V_{\kappa}^{x} + V_{\kappa}^{y} V_{\kappa}^{y} + g_0^E \frac{E^2}{\hbar \omega_{\kappa}} \]

\[ H_x \equiv J \hat{S}_x + h_x \]  

The electronic energy spectrum of the crystal is defined by the following equation

\[ (E + \Delta)[A^2P^2 + H_x^2 + h_z^2 - E(E + \Delta)] = 2APH_x h_z + \Delta H_x^2 \]  

Figure 1. Schematic presentation of the crystal energy levels (8).
If the external magnetic field $h_z$ is always small so that

$$h_z \ll H_x, \ AP, \ \Delta,$$

the energy levels could be found analytically in the first order in $h_z$ of the perturbation theory approximation

$$E_1 \approx -\Delta + \frac{2APH_xH_z}{E_0^2}$$

$$E_2 \approx -\frac{\Delta}{2}(1-\sqrt{1+a}) + \frac{APH_xH_z}{E_0^2 + \frac{\Delta^2}{4}(1+\sqrt{1+a})}$$

$$E_3 \approx -\frac{\Delta}{2}(1+\sqrt{1+a}) + \frac{APH_xH_z}{E_0^2 + \frac{\Delta^2}{4}(1-\sqrt{1-a})}$$

$$E_0 \equiv \sqrt{A^2P^2 + H_x^2}, \quad a \equiv \frac{4E_0^{2}}{\Delta^2}$$

In the paramagnetic and paradistortive crystal phase, at $T \geq T_m > T_s$, $P=0$, $H_x=h_z=0$ the energy level correspond to the accepted initially doublet-singlet structure

$$E_1 = -\Delta$$

$$E_2 = 0$$

$$E_3 = -\Delta.$$  \hspace{1cm} (10)

If the crystal temperature $T$ is below, but close to $T_m \approx T_s$, so that $a \ll 1$, $h_z \ll AP, H_x, \ \Delta$, the energy levels are described by the equations

$$E_1 \approx -\Delta + \frac{2APH_z}{E_0^2}$$
From the formulae (8)-(11) it is clear that the mixture of the electronic states allowing the existence of the vibronic magnetic moment is resulting from the interference of the Jahn-Teller molecular field $\Delta P$ and the magnetic molecular (or/and external) field. This leads to possible specific dynamics of the systems under consideration that will be discussed later.

Using the energy spectrum it is easy to calculate the homogeneous strain and the induced by the Jahn-Teller distortion average magnetic moment $M_z=g\beta\bar{S}_z$. Focusing on the vibronic magnetic moment we get

$$M_z = g\beta \frac{2\Delta P}{E_0} z^2 \left( e^{\frac{\Delta}{kT}} + \frac{1}{3} e^{\frac{2\Delta}{kT}} + \frac{E_0^2}{3E_0^2 + \Delta^2} e^{-\frac{E_0^2}{kT}} \right)$$

$$Z_0 = e^{\frac{\Delta}{kT}} \left( 1 + e^{\frac{4E_0^2}{\Delta kT}} \right) + e^{-\frac{E_0^2}{\Delta kT}}$$

Formula (13) demonstrates the vibronic origin of the magnetic moment

$$M_z \equiv M_{zvibr} \sim A \frac{V^2}{\hbar\omega}.$$  

3. Piezomagnetism, magnetic reorientation phase transitions, and multiferroicity.

The magnetic moment $M_z$ becomes different from zero only at $T<T_s$, when the structural ordering of the crystal takes place - $\bar{P} \neq 0$. As the homogeneous $U_{xz}$ strain is proportional to $\bar{P}$, the magnetic moment is linearly proportional to the homogeneous crystal strain – piezomagnetic effect. In other words the vibronic magnetism provides us with a microscopic mechanism of piezomagnetism with a piezomagnetic coefficient proportional to the square of the electron-phonon interaction.
constant. It is clear that for this mechanism of piezomagnetism the important role belongs to the cooperative Jahn-Teller effect.

With the lowering the temperature of the structurally ordered crystal phase the spontaneous monoclinic strain is increasing and so is the vibronic magnetic moment $M_z$. The total magnetic crystal moment that is the vector sum of the “regular” magnetic moment $\overrightarrow{M}_x$ and the vibronic moment $\overrightarrow{M}_z$ is deviating more and more from the initial a-axis direction perpendicular to the tetragonal z-axis of the crystal. This rotation of the spontaneous crystal magnetic moment is typical for the magnetic reorientation phase transitions. But in the case under the discussion the magnetic reorientation critical temperature $T_{\text{mreor}}$ is actually coincides with the critical $T_s$ temperature of the structural Jahn-Teller phase transition.

The angle of the magnetic moment rotation $\theta$ is described by the formulae

$$\tan \theta = \frac{\overrightarrow{S}_z}{\overrightarrow{S}_x} = \frac{AP\Delta}{E_0^2} \frac{F_1(A, J, h_z, T)}{F_2(A, J, H_x, T)}$$

$$F_1 = e^{\Delta kT} \left(1 + \frac{2E_0^2}{3} e^{\Delta kT}\right) + \frac{E_0^2}{3E_0^2 + \Delta^2} e^{\frac{E_0^2}{\Delta kT}}$$

$$F_2 = 2e^{\Delta kT} \left(1 + \frac{2E_0^2}{\Delta^2} \right) - e^{-\frac{E_0^2}{\Delta kT}}$$

As it follows from the equation (15) the tangent of the rotation angle is linearly proportional to the Jahn-Teller molecular field $A$.

If the Jahn-Teller crystal structural units or molecules are lacking the local center of space inversion simultaneously with the center of time inversion, the local distortions simultaneously are creating the vibronic magnetic and electric dipole moments. In this situation the cooperative Jahn-Teller effect is responsible for generating a magnetoelectric crystal state – Jahn-Teller multiferroic. Such a situation is experimentally observed in the tetragonal TbPO$_4$ crystals where the local symmetry of the Tb$^{3+}$ ions is $D_{2d}$, and the lowest electronic energy levels are a doublet and a singlet separated by a 2.2 cm$^{-1}$ gap. The difference between this real crystal situation and the microscopic model considered above is the antiferromagnetic (not ferromagnetic as in Hamiltonian (4)) ordering. This does not change qualitatively the results of the discussion, but below the structural phase
transition the crystal is ferroelastic, antiferroelectric, antiferromagnetic, not ferromagnetic.

In the TbPO₄ crystal J=-1.5 K, A=3.1 K and below the critical structural transition temperature Tₛ=2.15 K (Tₜₙ=2.28 K) there are 6 order parameters: $S_{za}$, $S_{xb}$, and $P_a$. At T<Tₛ each local monoclinic distortion creates an electric dipole moment along the crystal y-axis. However in the two crystal sublattices the dipole moments are antiparallel, so that the total spontaneous electric dipole moment is zero, and the total crystal cell with two Jahn-Teller centers in it remains centrosymmetric. It is easy to see that the external electric field $E$ along the y-axis disturbs the equivalence of the sublattices making the magnetoelectric coefficient

$$\alpha_{xy} = \frac{\partial M_x}{\partial E_y} \neq 0$$

at Tₛ<T<Tₚ. However at these temperatures naturally $\alpha_{zy} = \frac{\partial M_z}{\partial E_y} = 0$. At the same time at the temperatures below the structural phase transition both coefficients $\alpha_{xy}$ and $\alpha_{zy}$ are not zero. The results of the calculations are shown on the Figure 2.

**Figure 2.** Magnetoelectric coefficients in TbPO₄ crystals as a function of the temperature. 1 - $\alpha_{xy}$; 2 - $\alpha_{zy}$
The peculiarity of the Jahn-Teller multiferroics is related to the presence of the third – elastic – type of ordering additionally to magnetic and electric dipole moment orderings. As the elastic ordering is resulting from the cooperative Jahn-Teller effect, the virtual phonon exchange becomes fundamentally important for the effectiveness of the coupling between the magnetic and electric dipole moments. This leads to a very specific electron correlation in the systems under discussion. The electron correlation depends not only upon the magnetic moment correlation, but additionally upon the local distortion correlation. For example, in the considered above piezomagnetic Jahn-Teller multiferroics the electron correlation radius is the result of interference of the magnetic correlation radius and the virtual phonon exchange correlation radius. The relative contribution of the acoustic and optical phonons to the properties of the multiferroics becomes of big interest. As the experimental measurements of the electron correlation radius are possible (for example by the neutron scattering) there is a fundamentally important possibility to separate different mechanisms of multiferroicity. In part there is a hope to separate the crystal lattice mediated multiferroicity from the one induced by helicoidal magnetic structure.

The presence of three types of ordering in the Jahn-Teller multiferroics opens a variety of possibilities to dramatically change the state of the magnetic moments by the external electric field or the state of the electric dipole moments by the external magnetic field. For simplicity it is convenient once again to consider the ferroelastic antiferroelectric antiferromagnetic Jahn-Teller crystal of TbPO$_4$ type.

**a) ferroelastic-antiferroelectric-antiferromagnetic at** $\vec{E}_x = 0$

![Diagram](image_url)

**Figure 3.** Jahn-Teller multiferroics in external electric field.
As it is seen from the Fig.3 at the strong enough external electric field at T<T_s,T_N the electric dipole moments in one of the sublattices are overturned so that the transition from the antiferroelectric to the ferroelectric crystal state takes place. But this is accompanied by the structural transition from the ferroelastic to antiferroelastic state as in each of the sublattices the local strains and dipole moments are linearly proportional. At the same time due to piezomagnetism the overturn of the sublattice strain leads to the overturn of the vibronic magnetic moments so that the crystal is transferring from the antiferromagnetic state to the ferromagnetic one. It is clear that in Jahn-Teller multiferroics different interesting coupled metaelastic, metaelectric, and metamagnetic phenomena could be experimentally observed [7-11].

Conclusions.
1. The mechanism of vibronic magnetism is suggested.
2. It is shown that the Jahn-Teller effect could be considered as a basic microscopic mechanism of piezomagnetism.
3. The cooperative Jahn-Teller effect can explain the magnetic reorientation phase transitions in crystals.
4. The cooperative Jahn-Teller effect provides a microscopic model for multiferroicity. The specifics of Jahn-Teller multiferroics leads to an unusual electron correlation – interference of the magnetic and virtual phonon exchange interactions - that can be observed experimentally.
5. Crystal lattice vibrations mediate the strong coupling between the electric and magnetic dipole moments.

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