SUPEREXCHANGE ORDERING OF DEGENERATE ORBITALS AND MAGNETIC STRUCTURE OF DIELECTRICS WITH JAHN-TELLER IONS

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Submitted 12 April 1972
ZhETF Pis. Red. 15, No. 10, 629 - 632 (20 May 1972)

The crystalline and magnetic properties of substances containing ions with orbital degeneracy (for example, the ions d^4-Mn^{3+}, Cr^{2+}, d^9-Cu^{2+} in an octahedral surrounding) are usually explained by starting from the Jahn-Teller effect [1, 2]. The cooperative ordering of the orbitals and the lowering of the lattice symmetry is connected in such an approach with the elastic interaction of the local deformations near the different centers. The values of the corresponding interaction constants are usually unknown, and it is quite difficult to predict the concrete type of ordering.

We propose below another mechanism of cooperative ordering of the orbitals of Jahn-Teller ions, based on the superexchange interaction [3]. It becomes possible here, without making any additional assumptions, to obtain uniquely a type of orbital and magnetic structure that coincides with that obtained experimentally in a number of substances ($LaMnO_3$, $KCrF_3$, $KCuF_3$, MnF_3).

The possibility of superexchange ordering of orbitals was apparently first noted in [4]. This effect is considered, albeit without the very important interatomic-exchange factor and the concrete structure of the orbitals taken into account, also in [5].

The physical cause of the orbital ordering in this approach (in analogy with the usual ordering of the spins) is the fact that the lowering of the energy as a result of the virtual transitions of the electrons from center to center depends on the character of the filling of the orbitals on the neighboring centers.

We start from the usual description of the localized electrons with the aid of the Hamiltonian [3, 4]

$$H = \sum_{<i,j>\sigma, \alpha,\beta} b_{\alpha\beta}^{ij} a_{i\alpha\sigma}^{+} a_{j\beta\sigma} + \frac{U}{2} \sum_{\substack{i,\sigma,\sigma' \\ \alpha,\beta}} n_{i\alpha\sigma} n_{i\beta\sigma'}(1 - \delta_{\alpha\beta}\delta_{\sigma\sigma'}) -$$

$$- J \sum_{i,\sigma,\sigma'} a_{i1\sigma}^{+} a_{i1\sigma'} a_{i2\sigma'}^{+} a_{i2\sigma} . \tag{1}$$

We consider specifically the case of doubly degenerate orbitals (the index of the orbital is $\alpha = 1,2$) with one electron (or hole) per center. In the case of strong interaction, $b \ll U$, $J < U$, we can, in analogy with [3], change over to the equivalent "spin" Hamiltonian. Here, however, besides the spin degeneracy there is also orbital degeneracy. We shall characterize the orbital state by the "pseudospin" operator $\vec{\tau}$. It has all the properties of the operator of spin 1/2; the state $\tau^\zeta = +1/2$ corresponds to an occupied orbital $\alpha = 1$ (for example, d_{z^2}), and $\tau^\zeta = -1/2$ corresponds to $\alpha = 2$ ($d_{x^2-y^2}$). An arbitrary superposition of orbitals can be characterized by an angle θ in the (τ^ζ, τ^η) plane:

$$|\theta> = \cos\frac{\theta}{2}|d_{z^2}> + \sin\frac{\theta}{2}|d_{x^2-y^2}> .$$

The effective spin Hamiltonian is obtained by perturbation theory with respect to b/U; it is written out below accurate to terms J/U. In the simplest

case, when $b_{11} = b_{22} = b$ and $b_{12} = 0$ for any pair of nearest neighbors (e.g., in a bcc lattice), this Hamiltonian is given by

$$H_{eff} = \frac{b^2}{U} \sum_{<i,l>} \left\{ \left(1 - \frac{J}{U}\right)s_i \, s_l + \left(1 + 2\frac{J}{U}\right)\vec{\tau}_i \vec{\tau}_l - \frac{J}{U}\tau_i^\zeta \tau_l^\zeta + 4s_i \, s_l \times \right.$$

$$\left. \times \left(\vec{\tau}_i \vec{\tau}_l - \frac{J}{U}\tau_i^\zeta \tau_l^\zeta\right)\right\} . \tag{2}$$

It is easy here to analyze the situation to conclusion. The ground state at T = 0 is ferromagnetic with respect to spin and "antiferromagnetic" with respect to the pseudospin, i.e., the occupied orbitals 1 and 2 (or their linear combinations) alternate. At $T \neq 0$ we find that the magnetic order vanishes at $T_s \simeq b^2 J/U$, and the orbital order at $T_{orb} \simeq b^2/U$. In this case it is also easy to obtain the spectrum of the elementary excitations.

When the approach developed above is applied to concrete substances, it is necessary to take into account the explicit form of the corresponding orbitals. We have considered compounds with perovskite structure ($LaMnO_3$, $KCuF_3$, etc.), in which the Jahn-Teller ions form a primitive cubic lattice. The transition integrals $b_{\alpha\beta}^{ij}$ depend both on the indices α and β and on the mutual placement of the corresponding ions (see Table 2 of [3]). Taking into account the concrete form of $b_{\alpha\beta}^{ij}$, we can again write an effective Hamiltonian analogous to (2). It is, however, quite complicated, and to determine the ground state at T = 0 we can proceed in simpler fashion, by calculating directly the energies of the different structures for real $b_{\alpha\beta}^{ij}$. Thus, the contribution made to the energy from a pair of centers i, j with occupied orbitals α_i and α_j respectively and with empty orbitals β_i and β_j, at parallel spins, will be $E_{ij}^f = -(b_{\alpha_i \beta_j}^2 + b_{\alpha_j \beta_i}^2)/U$, and in the case of antiparallel spins we have $E_{ij}^{af} = -(b_{\alpha_i \beta_j}^2 + b_{\alpha_j \beta_i}^2 + 2b_{\alpha_i \alpha_j}^2)/U$.

It turned out that at small J/U the lowest energy is possessed by a magnetic structure consisting of ferromagnetic planes perpendicular to the c axis and coupled in antiferromagnetic fashion. The orbital structure is then as follows: In the plane perpendicular to c there are two sublattices with orbitals characterized by the angles $\theta = \pm(2\pi/3 + J/\sqrt{3}U)$, respectively, i.e., (at small J/U), the occupied orbitals $d_{z^2-x^2}$ and $d_{z^2-y^2}$ alternate. In the direction of the axis, two situations corresponding to the same energy are possible: located above the orbital $d_{z^2-x^2}$ is either the orbital $d_{z^2-y^2}$ (corresponding to anisotropic "τ-antiferromagnetism"), or a like orbital $d_{z^2-x^2}$ (chains ferromagnetic with respect to τ).

The magnetic and orbital structures obtained here correspond exactly to those experimentally observed in the aforementioned substances [1]. The presence of two types of orbitals (and consequently crystalline) ordering in $KCuF_3$ corresponding to the two equivalent types of τ-ordering described above, has been established in [6]. The theoretically obtained structure is quite nontrivial and its agreement with the experimental one can apparently serve as a weighty argument favoring the superexchange nature of not only the magnetic but also of the orbital ordering.

One more agrument favoring this premise is afforded by an analysis of the properties of the system at $T \neq 0$. It can be shown, first, that at the described type of ordering the magnetic properties turn out to be strongly

anisotropic and the antiferromagnetic coupling along the c axis is much stronger than the ferromagnetic coupling in the plane perpendicular to c; this has been observed experimentally in $KCuF_3$ [6]. Further, it follows from the developed theory that $T_s/T_{orb} \sim J/U$; usually $J/U \simeq 0.1$ [3]. In $LaMnO_3$ we actually have $T = 100°K$ and $T_{orb} \simeq 900°K$. A more detailed consideration of these questions, as well as all the details of the derivation of the results, will be published later.

Let us discuss the relation of the proposed mechanism to the ordinary Jahn-Teller effect. Generally speaking, these two mechanisms do not contradict each other: it is possible that the local distortions near the cation are determined by the Jahn-Teller effect, and their cooperative ordering by the superexchange considered above. In this case the ordering picture would be somewhat closer to the picture of Wojtowicz [7] (a transition of the order-disorder type) than to that of Kanamori [2].

It is possible that the mechanism considered here operates in substances with a different structure, for example in tetragonal spinels [1], and also in a number of rare-earth metal compounds (CeSb, DySB [8], $DyVO_4$ [9]), where a lattice transition has been observed at $T > T_s$.

In conclusion, we are grateful to L.N. Bulaevskii, V.L. Ginzburg, L.V. Keldysh, and V.L. Pokrovskii for useful discussions.

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SWITCHING MECHANISM IN AMORPHOUS SEMICONDUCTORS

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Submitted 12 April 1972
ZhETF Pis. Red. 15, No. 10, 632 - 635 (20 May 1972)

The switching effect in amorphous semiconductors, which has been under intense study in recent years (see, e.g., [1 - 3]), has not yet been uniquely and convincingly explained [4].

We propose here a switching mechanism that should take place in amorphous semiconductors if the model of [5] is valid for them.

According to this model, an amorphous (vitreous) semiconductor constitutes a system in which strong fluctuations in the spatial distribution of the charge give rise to such powerful fluctuations of the potential and of the potential energy of the electrons, that the corresponding bending of the energy bands turn out to be of the order of the width of the forbidden band of the superconducting material.

It is easily seen that under these conditions the semiconductor constitutes alternating n- and p-type regions, i.e., a system comprising a large number of