NEW MECHANISM OF ANISOTROPIC SUPEREXCHANGE INTERACTION

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(Received January 25, 1960)

Anisotropic exchange interaction as a combined effect of spin-orbit coupling and exchange interaction has been discussed by several authors.[1] These previous studies, however, were restricted to the so-called pseudo-dipolar coupling which is of second order in the spin-orbit coupling. The purpose of the present note is to provide a mechanism for an interaction of the form:

$$\vec{D}\cdot[\vec{S}_1\times\vec{S}_2], \tag{1}$$

which is linear with respect to the spin-orbit coupling, important in magnetic crystals of low symmetry, and generally much larger than the pseudo-dipolar coupling treated so far. Such an interaction was first suggested from purely symmetry grounds by Dzialoshinski.[2]

The theory is an extension of the superexchange theory to include the effect of spin-orbit coupling. A new formalism recently developed by Anderson[3] is used throughout the calculation. The one-electron states localized on the cations are expressed by Wannier functions and the one-electron Hamiltonian consists of the energy of the localized states and the transfer terms among them. We denote the two degenerate wave functions localized at the position R as follows:

$$\Psi_{n\uparrow}(r-R),\ \Psi_{n\downarrow}(r-R),$$

where ↑ and ↓ mean the spin almost up and almost down, respectively. Because of the spin-orbit coupling the spin-up and spin-down states are mixed in these wave functions. The one-electron terms of the Hamiltonian are written as

$$\begin{aligned} E = \sum_R\sum_n\sum_\sigma \epsilon_n(R)\alpha_{n\sigma}^*(R)\alpha_{n\sigma}(R) + \sum_{R\neq R'}\sum_{n,n'}\Big[& b_{n'n}(R'-R)\{\alpha_{n'\uparrow}^*(R')\alpha_{n\uparrow}(R)+\alpha_{n'\downarrow}^*(R')\alpha_{n\downarrow}(R)\} \\ & + C_{n'n}^{z}(R'-R)\{\alpha_{n'\uparrow}^*(R')\alpha_{n\uparrow}(R)-\alpha_{n'\downarrow}^*(R')\alpha_{n\downarrow}(R)\} \\ & + C_{n'n}^{-}(R'-R)\alpha_{n'\uparrow}^*(R')\alpha_{n\downarrow}(R)+C_{n'n}^{+}(R'-R)\alpha_{n'\downarrow}^*(R')\alpha_{n\uparrow}(R)\Big], \end{aligned} \tag{2}$$

where

$$\begin{aligned} b_{n'n}(R'-R)+C_{n'n}^{z}(R'-R) &= \int\Psi_{n'\uparrow}^*(r-R')H_1\Psi_{n\uparrow}(r-R)d\tau, \\ b_{n'n}(R'-R)-C_{n'n}^{z}(R'-R) &= \int\Psi_{n'\downarrow}^*(r-R')H_1\Psi_{n\downarrow}(r-R)d\tau, \\ C_{n'n}^{-}(R'-R) &= \int\Psi_{n'\uparrow}^*(r-R')H_1\Psi_{n\downarrow}(r-R)d\tau, \\ C_{n'n}^{+}(R'-R) &= \int\Psi_{n'\downarrow}^*(r-R')H_1\Psi_{n\uparrow}(r-R)d\tau, \end{aligned} \tag{3}$$

and

$$H_1 = \frac{p^2}{2m}+V(r)+\frac{\hbar}{2m^2c^2}\vec{S}\cdot[\operatorname{grad}V(r)\times\vec{p}],$$

$$C_{n'n}^{\pm}(R'-R) = C_{n'n}^{x}(R'-R)\pm iC_{n'n}^{y}(R'-R).$$

$\alpha_{n\uparrow}^*(R)$ and $\alpha_{n\uparrow}(R)$ are creation and annihilation operators of electrons in the state represented by $\Psi_{n\uparrow}(r-R)$, etc. The most important contribution to the superexchange arises from the configuration mixing of polar states due to the transfer terms of (2). The second order perturbation gives not only the ordinary isotropic coupling (b^2 terms) but an anisotropic coupling coming from bC terms: C^2 terms are much smaller than bC terms and make a contribution to the usual pseudo-dipolar coupling. We shall consider as an example the case of one electron per atom with the ground orbital state assumed to be nondegenerate, i.e., the orbital moment is quenched. The second order bC terms are calculated by using the relations:

$$\alpha_{n\uparrow}^{*}(R)\alpha_{n\uparrow}(R)-\alpha_{n\downarrow}^{*}(R)\alpha_{n\downarrow}(R)=2S_z(R),$$

$$\alpha_{n\uparrow}^{*}(R)\alpha_{n\downarrow}(R)=S_+(R),$$

and

$$\alpha_{n\downarrow}^{*}(R)\alpha_{n\uparrow}(R)=S_-(R),$$

for the occupied (ground) states. The empty states do not take part in the second order coupling. The result is as follows:

$$E_{R,R'}^{(2)}=\vec{\mathrm{D}}^{(2)}\cdot[\vec{\mathrm{S}}(R)\times\vec{\mathrm{S}}(R')],\tag{4}$$

where

$$\vec{\mathrm{D}}^{(2)}=\frac{4i}{U}[b(R-R')\vec{\mathrm{C}}(R'-R)-\vec{\mathrm{C}}(R-R')b(R'-R)],\tag{5}$$

the transfer integrals being those between the ground states of the ions at R and R', and U being the energy required to transfer an electron from an ion to its nearest neighbor, thus making a polar state. The transfer integrals b and C are calculated by using a perturbation method assuming that the orbital level separation in an ion is larger than the spin-orbit coupling. The b terms are the ordinary transfer integrals without spin-orbit coupling and the C terms are obtained, up to the first order in the spin-orbit coupling, as follows:

$$\vec{\mathrm{C}}(R'-R)=-\tfrac{1}{2}\lambda\left\{\sum_{m'}\frac{\vec{\mathrm{l}}_{m'n'}^{*}(R')}{\epsilon_{m'}(R')-\epsilon_{n'}(R')}b_{m'n}(R'-R)+\sum_{m}\frac{\vec{\mathrm{l}}_{mn}(R)}{\epsilon_{m}(R)-\epsilon_{n}(R)}b_{n'm}(R'-R)\right\}+\vec{\mathrm{c}}(R'-R),\tag{6}$$

where n, n' represent the ground orbitals and m, m' the excited orbitals, $\vec{\mathrm{l}}_{mn}(R)$ the matrix element of the orbital angular momentum of the ion at R, λ the spin-orbit coupling constant, and

$$\vec{\mathrm{c}}(R'-R)=\frac{\hbar}{4m^2c^2}\int\varphi_{n'}^{*}(r-R')[\operatorname{grad}V(r)\times\vec{\mathrm{p}}]\varphi_{n}(r-R)d\vec{\mathrm{r}},\tag{7}$$

$\varphi_n(r-R)$ being the ground orbital wave function.

From the third order perturbation, which includes transfer terms b and C between a singly occupied and an empty Kramers' doublet and the intra-atomic exchange interaction, we get the same type of coupling as (4). This term is J/U (J being the intra-atomic exchange energy) times as small as the second order term (4) as in the case of the ordinary superexchange.

The direct exchange coupling also has an anisotropic part of the form (4). The coupling constant is given by

$$\vec{\mathrm{D}}_{\mathrm{ex}}=-i\lambda\left\{\sum_{m}\frac{\vec{\mathrm{l}}_{mn}^{*}(R)-\vec{\mathrm{l}}_{mn}(R)}{\epsilon_{m}(R)-\epsilon_{n}(R)}J(nn'mn')-\sum_{m'}\frac{\vec{\mathrm{l}}_{m'n'}^{*}(R')-\vec{\mathrm{l}}_{m'n'}(R')}{\epsilon_{m'}(R')-\epsilon_{n'}(R')}J(nn'nm')\right\},\tag{8}$$

where

$$J(nn'mm')=\iint\varphi_{n}^{*}(r_1-R)\varphi_{n'}^{*}(r_2-R')\frac{e^2}{r_{12}}\varphi_{m}(r_2-R)\varphi_{m'}(r_1-R')d\vec{\mathrm{r}}_1d\vec{\mathrm{r}}_2.$$

It is interesting to note that all the terms treated above which are linear in the spin-orbit coupling have the form (1). This coupling vanishes when the symmetry of the crystal is high. For example, when there is only one magnetic ion in a unit cell and there is a center of inversion, or when there are two magnetic ions in a unit cell and a center of inversion is located halfway between them, this coupling vanishes. When the crystal symmetry is low, however, this coupling may be the most important anisotropic coupling between the spins. Though quantitative calculation of this coupling is very complicated, we can estimate the order of magnitude in relation to the isotropic superexchange. As is easily seen, all the three contributions to $\vec{D}$ treated above are roughly $(\Delta g/g)$ times the corresponding contributions to the isotropic superexchange interaction.[4] Though there may be some reduction of the magnitude, depending on the crystal structure, this coupling may well be $(g/\Delta g)$ times as big as the pseudo-dipolar anisotropic exchange. Extension of the theory to the case of many electrons per ion is generally complicated. We may expect the above rough order estimation is also valid in this case provided the orbital moment is quenched.

The possible existence of this type of coupling was first pointed out by Dzialoshinski[2] from symmetry considerations on some trigonal weak ferromagnets, α-Fe_2O_3, $MnCO_3$, and $CoCO_3$, though its origin was not clarified. Our mechanism gives the right orders of magnitude to explain the magnetic moments of α-Fe_2O_3, $MnCO_3$, and CrF_3.

This coupling is important not only in weak ferromagnetism but also in determining the spin arrangement in antiferromagnets of low symmetry. As an example we shall consider $CuCl_2 \cdot 2H_2O$, one of the most widely studied antiferromagnets. Because of the low crystal symmetry (space group is $V_h{}^7$) there is a coupling of the type (1) between the corner ion and the base-center ion; this type of coupling is absent between two ions both at the corner (base-center) sites. The magnitude of the coupling estimated from Δg is about 10% of the superexchange interaction and $\vec{D}$ is parallel to the b axis. Therefore, the antiferromagnetic spin arrangement in this crystal may be different from the one accepted at present, i.e., alternating ferromagnetic layers in the ab plane with the moment pointing in the a direction. We propose instead the arrangement shown in Fig. 1. The c component of a spin may be about 10% of the a component. We expect that this spin arrangement may give a more consistent understanding of the proton resonance data both above and below the Néel temperature[5] and the neutron diffraction data[6] for the position of the protons. Further details and related topics will be published later.

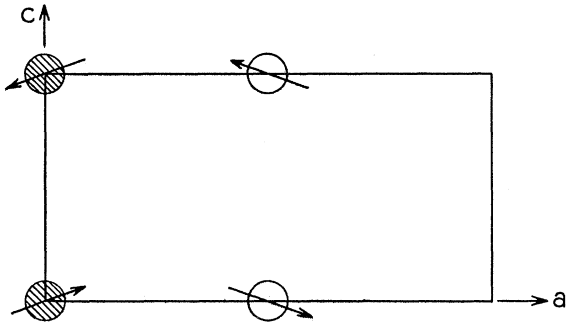

FIG. 1. A proposed spin arrangement in antiferromagnetic $CuCl_2 \cdot 2H_2O$. The spins are in the ac plane. The black and the open circles represent the ions at the positions 0, 0, 0 and $\frac{1}{2}, \frac{1}{2}, 0$, respectively.

I should like to thank Dr. P. W. Anderson for his continuous interest in this work.

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