SOVIET PHYSICS JETP VOLUME 25, NUMBER 2 AUGUST, 1967

NONLOCALIZED SPIN DENSITIES IN ANTIFERROMAGNETIC SUBSTANCES

Yu. GUFAN and I. E. DZYALOSHINSKIĬ

Institute of Theoretical Physics, Academy of Sciences, U.S.S.R.

Submitted to JETP editor September 22, 1966

J. Exptl. Theoret. Phys. (U.S.S.R.) 52, 604-610 (February, 1967)

A theory is proposed to describe the character of the variation of the spin density in the transition from the paramagnetic to the antiferromagnetic state. An essential feature is that, besides the deformations of the magnetic-ion form factor, which essentially conserve the local character of the spin, any such transition is accompanied by the appearance of a principally unlocalized part of the spin density. The order of magnitude of the effects is estimated.

RECENT advances in neutron-diffraction techniques, especially the use of polarized neutrons, make it possible not only to determine the direction of the spin of magnetic ions in antiferromagnets, but also to find directly the distribution of the average spin density $\mathbf{s}(\mathbf{r})$. An exact calculation of the coordinate dependence of $\mathbf{s}(\mathbf{r})$, on the basis of the microscopic theory, is quite difficult and the use of computers is mandatory. It is possible, however, to construct a simple theory which makes it possible in essence, using symmetry considerations only, to describe the character of the spin density distribution, to relate different dependences of $\mathbf{s}$ on the coordinates with the spin orientation, etc.

The situation is as follows: The (magnetic) symmetry of the crystal state resulting from the paramagnetic—ferromagnetic transition coincides as a rule with the symmetry of a crude scheme in which the spins are represented by arrows placed at the ion locations. The spin density corresponding to this scheme is of the form $\mathbf{s}(\mathbf{r}) = \Sigma_a \mathbf{s}_a \delta(\mathbf{r} - \mathbf{r}_a)$ (sum over all magnetic ions). However, the symmetry of such a coordinate dependence of $\mathbf{s}(\mathbf{r})$ (i.e., if we consider only the dependence of $\mathbf{s}(\mathbf{r})$ on the coordinates and assume that the vectors $\mathbf{s}_a$ are not rotated by the symmetry transformations[1]) may turn out to be higher than the magnetic symmetry of the crystal. Thus, for example, the magnetic symmetry of the antiferromagnetic $MnCO_3$, $CoCO_3$, Cr_2O_3, and α-Fe_2O_3 (in the high-temperature phase) belongs to the monoclinic system (see e.g.,[1]), and the symmetry of the indicated type of the coordinate dependence of $\mathbf{s}$ remains rhombohedral. This means that if we take into consideration the "smearing" of the spin density, then its coordinate dependence will in fact have the same symmetry as the crystal, i.e., it will also be monoclinic in our example.

We note that the change in the spin density cannot be reduced at all to a magnetostriction displacement of the ions themselves since such a displacement is proportional to $\mathbf{s}^2$, whereas the main change is proportional to the first power of the average spin (near the transition point).

The spin-density distribution in an antiferromagnet differs from the so-called magnetic form factor of the free ion in two respects. First, the form factor of the ion is distorted by the interaction of the spin with the crystal field, which in general is trivial. Second, it is distorted by exchange and relativistic interactions with other magnetic ions. As we shall show later, such interactions can lead not only to a more appreciable distortion of the form factor, but even to a shift of the center of gravity of the spin distribution relative to the nucleus.

We should thus consider a density $\mathbf{s}$ of the most general form. The characteristic features of the spin density $\mathbf{s}(\mathbf{r})$ are easiest to explain by expanding it in irreducible representations of the symmetry group of the paramagnetic phase. It is convenient here to separate from the very outset the coordinate dependence of $\mathbf{s}$ in explicit form, and to expand $\mathbf{s}(\mathbf{r})$ in terms of functions $\varphi_{n\alpha}(\mathbf{r})$ that depend on the coordinates only[2]:

$$s_i(\mathbf{r}) = \sum_{n\alpha} S^i_{n\alpha} \varphi_{n\alpha}(\mathbf{r}), \quad i = x, y, z. \tag{1}$$

---

[1] This corresponds to the usual method of representing an antiferromagnet in the form of a lattice with pluses and minuses at the lattice points.

[2] More details on the expansion if $\mathbf{s}(\mathbf{r})$ in functions of irreducible representations are found in [2], Sec. 2.

Here n numbers the irreducible representation and α the function of its basis. The coefficients $S^i_{n\alpha}$ are transformed in accordance with a representation that is a direct product of the representation n by the representation that transforms the coordinate-independent pseudovector. The latter is in general reducible; different linear combinations of the quantities $S^i_{n\alpha}$ transform in accordance with irreducible representations (for a given n). We shall henceforth frequently write $S^i_{n\alpha}$ in the form of a "vector" $\mathbf{S}_{n\alpha}$:

$$\mathbf{s}(\mathbf{r}) = \sum_{n\alpha} \mathbf{S}_{n\alpha}\varphi_{n\alpha}(\mathbf{r}). \qquad (2)$$

To find $\mathbf{S}_{n\alpha}$ we shall use the Landau theory of second-order phase transitions[3] (see also[1,2]). We shall carry out the calculations by using as examples the theoretically and experimentally well investigated crystallographically isomorphic α-Fe_2O_3, Cr_2O_3, $CoCO_3$, and $MnCO_3$. In these crystals, as is well known, the phase transition occurs without a change in the unit cell, so that the summation in (2) is only over functions that are periodic and have the same period as the crystal. It is sufficient to consider as the symmetry group of the paramagnetic phase the group D^6_{3d}/T, which is obtained from the crystal symmetry group D^6_{3d} if all the translations T are regarded as identity transformations. The group D^6_{3d}/T is isomorphic to the rhombohedral group D_{3d} and differs from the latter in that certain axes and symmetry planes are replaced by screw axes and slip planes.

By virtue of the noted isomorphism, the irreducible representations of interest to us, of the symmetry group of the paramagnetic phase, coincide with the representations of the x group D_{3d}. The latter has six irreducible representations (see[4] for notation): three even, of which two (A_{1g}, A_{2g}) are one-dimensional and one (E_g) is two-dimensional, and respectively three odd ones, A_{1u}, A_{2u}, and E_u. We denote the functions $\varphi_{n\alpha}$ corresponding to these representations as follows:

$$\varphi_{A_{1g}} = M; \quad \varphi_{A_{2g}} = W; \quad \varphi_{E_{g1}} = U, \quad \varphi_{E_{g2}} = V;$$
$$\varphi_{A_{1u}} = P; \quad \varphi_{A_{2u}} = Z; \quad \varphi_{E_{u1}} = X, \quad \varphi_{E_{u2}} = Y.$$

The function P is a pseudoscalar, and the functions X, Y, and Z transform like the corresponding components of a polar vector. In turn, M is a scalar and U, V, and W are components of a pseudovector. The "vectors" S corresponding to these functions will be denoted

$$\mathbf{M};\ \mathbf{W};\ \mathbf{U}, \mathbf{V};\ \mathbf{P};\ \mathbf{Z};\ \mathbf{X}, \mathbf{Y}. \qquad (3)$$

It is instructive to compare these results with the theory previously developed by one of the authors[1] for the antiferromagnetism of the crystals under consideration, in which the spins of the magnetic ions were assumed to be fully localized. Comparison shows that the character of the transformations of M coincides with that of m from[1], and analogously $\mathbf{W} = \mathbf{l}_1$, $\mathbf{P} = \mathbf{l}_2$, and $\mathbf{Z} = \mathbf{l}_3$. On the other hand, there are no densities of the type U, V or **X**, **Y** in the pointlike picture.

The representations corresponding to the "vectors" (3) are reducible. Their following combinations transform in accordance with irreducible representations:[3)]

$$\begin{aligned}
A_{1g}&:\quad W_z;\ U_x + V_y,\\
A_{2g}&:\quad M_z;\ U_y - V_x,\\
E_g&:\quad (M_x, M_y);\ (W_x, W_y);\ (U_z, V_z);\ (U_y + V_x, U_x - V_y),\\
A_{1u}&:\quad Z_z;\ X_x + Y_y,\\
A_{2u}&:\quad P_z;\ X_y - Y_x,\\
E_u&:\quad (P_x, P_y);\ (Z_x, Z_y);\ (X_z, Y_z);\ (X_y + Y_x, X_x - Y_y).
\end{aligned}$$

We shall show now that just as establishment of purely antiferromagnetic order in α-Fe_2O_3, $CoCO_3$, and $MnCO_3$ (described by the "vector" **W**) involves weak ferromagnetism (vector **M**), the establishment of antiferromagnetic order leads to the appearance of a principally nonlocal part of the spin density, described by "vectors" U and V. To this end we write out, as in[1], the most general form of the second-order terms in the expansion of the thermodynamic potential Φ in powers of M, W, ... :

$$\begin{aligned}
\Phi = {} & \Phi_0 + {}^1/_2 A\mathbf{W}^2 + {}^1/_2 B\mathbf{M}^2 + {}^1/_2 C(\mathbf{U}^2 + \mathbf{V}^2) + {}^1/_2 aW_z^2\\
& + {}^1/_2 bM_z^2 + {}^1/_2 c_1(U_z^2 + V_z^2) + {}^1/_2 c_2(U_x + V_y)^2\\
& + {}^1/_2 c_3(U_y - V_x)^2 + \alpha(W_xM_y - W_yM_x) + \beta(W_xU_z\\
& + W_yV_z) + \gamma\,[W_x(U_y + V_x) + W_y(U_x - V_y)]\\
& + \delta W_z(U_x + V_y) + \varepsilon(M_xV_z - M_yU_z)\\
& + \varkappa[M_x(U_x - V_y) - M_y(U_y + V_x)] + \lambda M_z(U_y - V_x)\\
& + \mu[(U_x - V_y)V_z + (U_y + V_x)U_z]. \qquad (4)
\end{aligned}$$

The first three terms of the expansion (the coefficients A, B, and C) are due to exchange interaction. They do not change when all the spins in the crystals are rotated through the same angle. The remaining terms are connected in one manner or another with relativistic interactions.

The expansion of Φ in powers of **P**, **Z** and **X**, **Y** coincides exactly with (4) if we replace in the latter M by P, W by Z, and U, V by X, Y.

The presence in (4) of mixed terms (coefficients α, β, ...) shows that the occurrence of pure-antiferromagnetic order (**W**) causes appearance of all

---

[3)] We use here and throughout a rectangular coordinate system with the z axis directed along the crystal and the x axis directed along one of the twofold axes.

the remaining components of the spin density-weak ferromagnetism (M) and the unlocalized parts (U, V). The latter can be obtained by minimizing (4) at a specified W, the magnitude of which is determined by the fourth-order terms (see[1]). In the high-temperature phase of α-Fe_2O_3 and in $MnCO_3$ and $CoCO_3$, where W lies in the basal plane, we have[4]

$$M_x = \frac{\alpha}{B} W_y, \quad M_y = -\frac{\alpha}{B} W_x, \quad M_z = 0.$$
$$U_x = -\frac{\gamma}{C} W_y, \quad U_y = -\frac{\gamma}{C} W_x, \quad U_z = -\frac{\beta}{C} W_x,$$
$$V_x = -\frac{\gamma}{C} W_x, \quad V_y = \frac{\gamma}{C} W_y, \quad V_z = -\frac{\beta}{C} W_y. \tag{5}$$

In the low-temperature α-Fe_2O_3 phase and in $FeCO_3$ we have

$$\mathbf{M} = 0,$$
$$U_x = -\frac{\delta}{C} W_z, \quad U_y = U_z = 0,$$
$$V_y = -\frac{\delta}{C} W_z, \quad V_x = V_z = 0. \tag{6}$$

We note that in the low-temperature phase of α-Fe_2O_3 and in $FeCO_3$ the nonlocal character of the density leads to the occurrence of average-spin components lying in the basal plane, something which cannot occur at all in the case of a strictly localized spin.

It is seen from the structure of expressions (4), (5), and (6) that the appearance of M and of U, V is connected with weak relativistic interactions. Therefore (see[1]) relations (5) and (6) remain in force also far from the transition point, provided W in (5) and (6) is now taken to mean a unit vector in the direction of W.

Relations for the case of Cr_2O_3 are obtained from (5) and (6) by replacing in them W, M, U, and V by P, Z, X, and Y, respectively.

The presence of nonlocalized components U, V of the spin density causes the coordinate dependence of $\mathbf{s}(\mathbf{r})$ to lose the trigonal symmetry which would remain in force in the pointlike picture ($U = V = 0$; $M, W \neq 0$). The symmetry of the dependence of s on the coordinates becomes monoclinic. In particular, the intensities of the elastic neutron scattering ($l$mn) peaks lose their symmetry with respect to cyclic permutation l → m → n.

We shall now analyze in greater detail the character of the dependence of the functions M, W, U, and V on the coordinates in the vicinity of the magnetic ion Fe^{3+} in α-Fe_2O_3, writing out for this purpose the general form of their expansion in powers of the distance from this ion. In α-Fe_2O_3, the four iron ions lie on the crystal axis in the positions (uuu), ($\overline{uuu}$), ($\frac{1}{2}$ + u, $\frac{1}{2}$ + u, $\frac{1}{2}$ + u), and ($\frac{1}{2}$ − u, $\frac{1}{2}$ − u, $\frac{1}{2}$ − u). These positions have an intrinsic symmetry C_3, so that these expansions should be invariant to rotations about a threefold axis. They are of the form[5]

$$M, W = M_0, W_0 + az + bz^2 + c(x^2 + y^2) + dx(x^2 - 3y^2)$$
$$+ ey(3x^2 - y^2) + fxz(x^2 - 3y^2) + gyz(3x^2 - y^2) + \ldots; \tag{7}$$

$$U = a'x + b'(x^2 - y^2)$$
$$+ c'yz - 2d'xyz + e'(x^4 - 6x^2y^2 + y^4) + \ldots, \tag{8}$$
$$V = a'y - 2b'xy + c'xz + d'z(x^2 - y^2) + 4e'xy(x^2 - y^2).$$

The expansions of the functions P, Z, X, Y in the vicinities of the Cr^{3+} ion in Cr_2O_3 have exactly the same form.

The expansion (7) for M and W has two types of terms. The first are even in x, y, and z and represent the distortions of the free-ion form factor by the interaction with the crystal field, the fourth-order term, in particular, was investigated by Kaplan[5]). The second are odd and describe the less trivial distortions of the form factor (loss of inversion) as well as the shift of the center of gravity of the spin distribution in the direction of the crystal axis away from the nucleon (the term proportional to z). These terms are connected, as will be shown below, with the interaction between the considered magnetic ion and the other ions.

All the terms of the expansion (8), both even and odd, describe the violation of the trigonal symmetry of the form factor. In addition, the presence of terms proportional to x or y indicates a shift of the center of gravity of the spin-density distribution in the basal plane. As already indicated, the appearance of U and V is connected with the spin-spin interaction between different ions.

Let us estimate now the order of magnitude of the considered effects. The appearance of a nonlocalized spin density is due essentially to the interaction of the given ion with the neighbors, or more accurately speaking, with the inhomogeneity

---

[4] We have left out of (5) and (6) small corrections due to the small terms (the coefficients b, c_1, c_2, c_3, ϵ, κ, λ, μ) in (4), which are proportional (after substituting (5) and (6)) to the third power of the relativistic coefficients (a^2b, c_γ^2, $\lambda a\gamma$, etc.)

[5] We do not write out the trivial terms that result from the expansion of the coefficients of the lower-order terms in powers of z^2 and $x^2 + y^2$. The coefficients in formula (7) are of course different from M and W.

of the effective magnetic field acting on the spin of the electrons belonging to the ion under consideration. This effective field can be introduced in the following fashion: We consider the effective energy E_{eff} of the interaction between the magnetic ions, expressed in terms of the average spin density [6] $\mathbf{s}(\mathbf{r})$

$$E_{eff}=\frac{1}{2}\int J(\mathbf{r}-\mathbf{r}')\mathbf{s}(\mathbf{r})\mathbf{s}(\mathbf{r}')\,d\mathbf{r}\,d\mathbf{r}' +\frac{1}{2}\int Q_{ik}(\mathbf{r}-\mathbf{r}')s_i(\mathbf{r})s_k(\mathbf{r}')\,d\mathbf{r}\,d\mathbf{r}', \tag{9}$$

where the first term represents the exchange energy and the second the energy of the spin-spin interaction; it is obvious that $Q \sim v^2/c^2$, where v is the velocity of the electrons in the atom. Then the effective field $\mathcal{H}(\mathbf{r})$ is defined as $\delta E_{eff}/\delta\mathbf{s}(\mathbf{r})$, i.e.,

$$\mathcal{H}_i(\mathbf{r})=\int J(\mathbf{r}-\mathbf{r}')s_i(\mathbf{r}')\,d\mathbf{r}'+\int Q_{ik}(\mathbf{r}-\mathbf{r}')s_k(\mathbf{r}')\,d\mathbf{r}'.$$

In this expression we can replace in first approximation the exact spin density **s** by its pure-antiferromagnetic component W which would be obtained in the pointlike-spin system (we denote it W_0):

$$\mathcal{H}_i(\mathbf{r})=\int J(\mathbf{r}-\mathbf{r}')W_{0i}\,d\mathbf{r}'+\int Q_{ik}(\mathbf{r}-\mathbf{r}')W_{0k}\,d\mathbf{r}'. \tag{10}$$

The Hamiltonian of the interaction of the ion under consideration with this field is

$$\hat{H}=-\sum_a\mathcal{H}(\mathbf{r}_a)\hat{\mathbf{s}}_a, \tag{11}$$

where the summation is over the electrons of the unfilled d-shell, and the corresponding additions to the spin-density can be calculated with the aid of the perturbation-theory formula for the wave function

$$\Psi_0=\Psi_0^{(0)}+\sum_n\frac{H_{0n}\Psi_n^{(0)}}{E_0-E_n}. \tag{12}$$

To estimate the order of magnitude of the matrix elements H_{0n} of the perturbation, let us expand the effective field in powers of the distance from the nucleus. The constant terms, of course, make no contribution to the nonlocal part of the spin density and therefore is of no interest to us. The integral determining the exchange part of the effective field is invariant to the proper symmetry group of the ion position, and therefore its series expansion has the same form as (7). The spin-spin part of the effective field is not invariant with respect to C_3, so that its expansion contains in addition also all the terms contained in (8).

The nonlocal parts of interest to us are odd functions of the coordinates and as such they can arise only under the influence of an odd component of the effective field. This means that in this case the only nonvanishing matrix elements H_{0n} are those between states with different parity (i.e., different configurations, for example $d^6 \to d^5p$ in the case of the Fe^{3+} ion). The nonlocal part of the density W_{nl} is proportional to

$$W_{nl}\sim\frac{\Psi_0^{(0)}H_{0n}\Psi_n^{(0)}}{E_0-E_n},$$

hence

$$W_{nl}\sim\frac{\Theta}{\varepsilon_0}W_0, \tag{13}$$

where Θ is the transition temperature and ϵ_0 is a quantity on the order of the atomic energy. For M_{nl} we have the estimate

$$M_{nl}\sim\frac{\Theta}{\varepsilon_0}M_0, \tag{14}$$

where M_0 is the spontaneous moment. Formula (14) is obtained if all the reasoning regarding the exchange part of the effective fields is applied to the effective field resulting from the antisymmetrical exchange mentioned in footnote 6.

For U and V we obtain in accord with the foregoing the following general estimate:

$$U,\ V\sim\frac{v^2}{c^2}W_0. \tag{15}$$

It must only be kept in mind that actually those parts of U and V which are odd in the coordinates may turn out to be much smaller than the even parts, for in the former case the denominators in (12) contain the differences between the configuration energies, and in the latter they contain as a rule much smaller quantities.

In the case of $MnCO_3$, $CoCO_3$, and $FeCO_3$ the magnetic ions are in positions ((000) and (½ ½ ½)) having the symmetry C_{3i}. Therefore all the terms of (7) and (8) that are odd in the coordinates vanish. In particular, in these substances there should be no shift in the center of gravity of the distribution of the magnetic moment.

In metallic antiferromagnets there exists a special mechanism connected with the polarization of the conduction electrons. It is necessary here to take into account the character of the interaction between the s-electron and the magnetic ion (the Condo effect). An examination of these questions, however, is outside the scope of the present article.

---

[6] We have purposely left out from this expression the antisymmetrical-exchange term introduced by Moriya and one of the authors and causing the weak ferromagnetism of the compounds in question, since it adds nothing new compared with the pure exchange term.

---

[1] I. E. Dzyaloshinskiĭ, JETP **32**, 1547 (1957), Soviet Phys. JETP **5**, 1259 (1957); Phys. Chem. Solids **4**, 241 (1958).

[2] I. E. Dzyaloshinskiĭ, JETP **46**, 1420 (1964), Soviet Phys. JETP **19**, 960 (1964).

[3] L. D. Landau and E. M. Lifsthitz, Statisticheskaya fizika (Statistical Physics), Nauka, 1964.

[4] L. D. Landau and E. M. Lifsthitz, Kvantovaya mekhanika (Quantum Mechanics), Fizmatgiz, 1963.

[5] T. A. Kaplan, Phys. Rev. **A136**, 1036 (1965).

Translated by J. G. Adashko
75