Anisotropy of exchange interaction

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A Hamiltonian for the exchange interaction between two atoms that contains both isotropic and anisotropic terms is derived on the basis of a method that is a synthesis of the apparatus of second quantization and the technique of irreducible tensor operators. A detailed study is made of the anisotropy of the Hamiltonian, which is due to the asymmetry in the electron-density distribution of the interacting pair of atoms, the influence of the crystal field, the effect of the spin-orbit coupling in them, and the diverse orientations of the direction of the pair with respect to the crystallographic axes. The existence of a "latent" anisotropy, which can lead to different signs for the Heisenberg exchange parameter for differently-oriented identical pairs, is discovered in the case of atoms in orbitally nondegenerate states. An attempt is made to explain the magnetic properties of metallic scandium with the aid of the results.

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It is known at present from experimental[1-3], as well as theoretical[4-13], investigations that the exchange interaction between atoms in degenerate orbital states is anisotropic in nature. Nevertheless, a detailed investigation of all the possible sources of anisotropy has thus far not been carried out. Only specific causes that can lead to an anisotropy in either the final or the intermediate Hamiltonian have been analyzed.

In particular, it has been shown in a number of papers[12,14] that in the case of the rare-earth elements and the elements of the iron group with incompletely "quenched" orbital angular momenta the anisotropic exchange interaction between the effective spins can be obtained from the Heisenberg isotropic exchange interaction if the spin-orbit coupling and the effect of the crystal field are taken into account. In its turn, the exchange Hamiltonian, which contains the operators of the true spin angular momenta of the interacting atoms, also turns out to be anisotropic, and its anisotropy may be due to the asymmetry in the electrostatic interactions between the magnetic ions and the diverse orientations of the pair axis with respect to the crystallographic axes[11,12].

The anisotropy of the electrostatic interactions between two centers has been investigated by Levy and Copland[10,12] in the one-electron-per-center model. An attempt to study it in the many-electron case has been undertaken by Druzhinin and Moskvin[11]. However, owing to the non-orthogonality of the initial wave functions and the loss in this connection of a number of important terms, these investigations could not be carried through.

In the present paper we obtain on the basis of the self-consistent many-electron theory of interaction between atoms in crystals developed in[13,15-17] a Hamiltonian for the direct exchange interaction which contains the actual spin and orbital angular momenta of the interacting atoms. The anisotropy of the Hamiltonian, which owes its origin to the asymmetry in the electron-charge distribution in the ions and the orientation of the pair with respect to the crystallographic axes, is investigated in detail. Then, using as an example the ions Sc^{2+} in a hexagonal lattice, we analyze the exchange anisotropy that is due to the crystal field and the spin-orbit coupling. Finally, we make an attempt to understand the magnetic properties of metallic scandium on the basis of the obtained results.

1. THE EXCHANGE-INTERACTION HAMILTONIAN

Let us consider a system of two atoms, one of which—with N_1 electrons and a nuclear charge Z_a—is located at the point a, while the second—with N_2 electrons and a nuclear charge Z_b—is located at the point b. Let us write their interaction Hamiltonian in the form

$$V=-\sum_{i=1}^{N_1}\frac{Z_b}{r_{bi}}-\sum_{j=1}^{N_2}\frac{Z_a}{r_{aj}}+\sum_{ij}^{N_1,N_2}\frac{1}{r_{ij}},\tag{1}$$

where the first term describes the interaction of the electrons of the first atom with the nucleus of the second atom. The second term has an analogous meaning, while the third term characterizes the electrostatic interaction of the electrons of one atom with the electrons of the other.

Further, if we use the results obtained in[17], then this Hamiltonian can be written in an equivalent second-quantized form, from which it is not difficult in the case of atoms having only one open shell to go over to double irreducible tensor operators of the one- and two-electron types[18].

Before writing down the transformed form of the Hamiltonian, let us simplify the problem even further by assuming that the wave functions of the filled shells overlap only slightly with each other and with the wave functions of the unfilled shells. Such an assumption leads to an appreciable simplification of the form of the exchange parameters and is, in essence, equivalent to going over to the model in which it is assumed that the electrons of the unfilled shell of each atom move in the field of cores with charges Z produced by the nuclei and all the electrons of the filled inner shells. To assume the charges Z to be equal to the sum of the number of electrons in the unfilled shell and the valency of the atom in the crystal is, however, scarcely practical. It is apparently more reasonable to find the corresponding quantities Z from the following arguments. The use as the initial Hamiltonian of terms characterizing only the interaction (1) between the atoms can be considered to be mathematically correct[15,16] only in the case when the wave functions of the initial approximation are eigenfunctions of the zeroth-order Hamiltonian

$$\mathcal{H}_0=-\sum_i\frac{\Delta_i}{2}-\sum_j\frac{\Delta_j}{2}-\sum_i\frac{Z_a}{r_{ai}}-\sum_j\frac{Z_b}{r_{bj}}+\sum_{ik}\frac{1}{r_{ik}}+\sum_{jl}\frac{1}{r_{jl}},$$

which includes the electron kinetic energy operators and the interaction of the electrons with their own nuclei and with other electrons of their atom. But the real functions with which we must, in practice, carry out the computations do not naturally possess such a property, and therefore there appear in the exchange parameters nonzero terms arising from the intratomic interactions of the Hamiltonian $\mathscr{H}_0$. By requiring that such terms vanish, we can, on the one hand, improve the initial wave functions and, on the other, obtain relations for the determination of the effective charges Z.

An analogous procedure has been used before by Freeman and Watson[19] to determine Z in the case of the one-electron model. Let us now turn our attention to the fact that all the operators figuring in (1) do not depend on the spin variables. This allows us in the resulting expression to perform the summation over the spin components and, in the case when the states of the configuration are limited by the limits of only the terms of maximum multiplicity, to go over from the double irreducible tensors to products of spin and orbital tensor operators.

Let us omit the details of this transition, and write down the final expression:

$$\mathscr{H}_{\text{ex}}=\left[\frac{1}{2}+\frac{1}{2S_1S_2}(\mathbf{S}_1\mathbf{S}_2)\right]\sum_{k_1q_1k_2q_2}\Big(J_{q_1q_2}^{k_1k_2}V_{q_1}^{k_1}V_{q_2}^{k_2}$$
$$+\sum_{k_1'k_1''}J_{q_1q_2}^{(k_1'k_1'')k_1k_2}V_{q_1}^{(k_1'k_1'')k_1}V_{q_2}^{k_2}+\sum_{k_2'k_2''}J_{q_1q_2}^{k_1(k_2'k_2'')k_2}V_{q_1}^{k_1}V_{q_2}^{(k_2'k_2'')k_2}\Big), \qquad (2)$$

in which the S_i denote the spins of the interacting atoms and the symbols V_q and $V_q^{(k'k'')k}$ denote orbital irreducible tensor operators of the one- and two-electron types. The quantities J are constants that depend on a large number of all sorts of two-center integrals. The explicit expressions for them are unwieldy, and we shall not give them here.

In deriving the Hamiltonian (2) we assumed that the axes of the coordinate systems localized at the centers a and b are oriented parallel to each other. The numerous two-center integrals figuring in the parameters J are most easily computed if, moreover, the z axes of both systems are directed along the line joining the nuclei of the interacting atoms. For such a choice of the axes, q_2 can be equal only to $-q_1$, and the quantities J will possess the properties

$$J_{q-q}^{k_1k_2}=(-1)^{k_1+k_2}J_{-qq}^{k_1k_2},\qquad J_{q-q}^{k_1k_2}=J_{-qq}^{k_1k_2}, \qquad (3)$$
$$J_{q-q}^{(k_1'k_1'')k_1k_2}=(-1)^{k_1'}J_{q-q}^{(k_1'k_1'')k_1k_2},\qquad J_{q-q}^{(k_1'k_1'')k_1k_2}=(-1)^{k_1''+k_2}J_{q-q}^{(k_1'k_1'')k_1k_2},$$

from which it follows that k_1', k_2', $k_1''+k_2$, $k_2''+k_1$, and k_1+k_2 should be even numbers, while from the condition that the matrix elements of the one- and two-electron tensor operators should not vanish follows the restriction of all the ranks to within the range of from 0 to $4l$.

In practical applications of the Hamiltonian (2), however, it is much more convenient to choose the coordinate systems with the axes aligned along the axes of the local crystal fields of the individual atoms. The necessary transformation of the Hamiltonian can easily be carried out with the aid of the transformation laws for irreducible tensor operators.

Let us, for the sake of simplicity, consider the first term in (2) and transform each of its operators according to the law (see[20])

$$V_q^k=\sum_{q'}D_{q'q}^{(k)}\{\alpha,\beta,\gamma\}\,V_{q'}^{k}, \qquad (4)$$

where the V_q^k are the tensor components in the old (the z axis along the axis of the pair), and the $V_{q'}^k$ the components in the new, coordinate system and the $D_{q'q}^{(k)}\{\alpha,\beta,\gamma\}$ are the elements of the matrix representative, in the irreducible rotation-group representation, of the rotation operator consisting of the successive rotations of the old coordinate systems through the angle γ about the z axis, then through the angle β about y′, and, finally, through the angle α about the z″ axis. Further, using the relation (1.38) in[21], we shall have for the transformed part of the Hamiltonian the expression

$$\Sigma(2k+1)\begin{pmatrix}k_1 & k_2 & k\\ q_1' & q_2' & q'\end{pmatrix}\begin{pmatrix}k_1 & k_2 & k\\ q & -q & 0\end{pmatrix}D_{q'0}^{(k)*}V_{q_1'}^{k_1}V_{q_2'}^{k_2}J_{q-q}^{k_1k_2}, \qquad (5)$$

where the summation is performed over all the indices. Performing the summation over q_1' and q_2', and then summing, in accordance with the equality

$$J_0^{(k_1k_2)k}=\sum_q(2k+1)^{1/2}(-1)^{k_2-k_1}\begin{pmatrix}k_1 & k_2 & k\\ q & -q & 0\end{pmatrix}J_{q-q}^{k_1k_2}, \qquad (6)$$

over q, we obtain in place of (5) the expression

$$\sum J_0^{(k_1k_2)k}\{V^{k_1}V^{k_2}\}_{q'}^{(k)}D_{q'0}^{(k)}. \qquad (7)$$

To accomplish the necessary transformation, let us rotate the coordinate systems first about the old z axes through an angle γ such that the y′ axes lie in the x‴y‴ planes, then about the y′ axes through an angle θ such that the direction of $\mathbf{R}_{ab}$ coincides with the axes z‴, and, finally, through the angle $\pi-\varphi$ about the axis z‴, where φ is the angle the component of $\mathbf{R}_{ab}$ in the x‴y‴ plane makes with the x‴ axis. Then using the relation (A.10) from[20], we obtain

$$D_{q'0}^{(k)*}\{\pi-\varphi,\theta,\gamma\}=\left\{\frac{4\pi}{2k+1}\right\}^{1/2}Y_k^{q'}(\theta,\varphi)=C_{q'}^{k}(\theta,\varphi), \qquad (8)$$

where $C_q^k(\theta,\varphi)$ is a spherical-function operator in which the angles θ and φ are the spherical angles of the direction $\mathbf{R}_{ab}$ of the axis of the pair in the new systems of coordinates x‴, y‴, z‴.

Using (8), performing the summation over q′ in (7), and then carrying out analogous transformations with the remaining terms in (2), we can transform the entire exchange Hamiltonian into the form

$$\mathscr{H}_{\text{ex}}=\left[\frac{1}{2}+\frac{1}{2S_1S_2}(\mathbf{S}_1\mathbf{S}_2)\right]\sum_{k_1k_2k}\Big[J_0^{(k_1k_2)k}(\{V^{k_1}V^{k_2}\}^kC^k(\theta,\varphi))$$
$$+\sum_{k_1'k_1''}J_0^{((k_1'k_1'')k_1k_2)k}(\{V^{(k_1'k_1'')k_1}V^{k_2}\}^kC^k(\theta,\varphi))$$
$$+\sum_{k_2'k_2''}J_0^{(k_1(k_2'k_2'')k)}(\{V^{k_1}V^{(k_2'k_2'')k_2}\}^kC^k(\theta,\varphi))\Big], \qquad (9)$$

where the round brackets denote the scalar products of the tensor operators.

2. THE EXCHANGE ANISOTROPY DUE TO THE ASYMMETRY OF THE WAVE FUNCTIONS OF THE INTERACTING ATOMS

For the analysis of the general properties of the anisotropy of this Hamiltonian, it probably makes sense to consider further the simplest system for which such an anisotropy is, in principle, possible. Examples of suitable systems are pairs of identical atoms of the elements of the iron group when the unfilled shell of each of the atoms contains one d electron. The restriction of the investigation to d electrons leads to a situation in which the quantities k_1 and k_2 cannot exceed 4 and the resulting ranks of the tensor products and the spher-

The parameters $\tilde{J}_0^{(k_1k_2)k} = [(2k_1+1)(2k_2+1)]^{1/2} J_0^{(k_1k_2)k}$ (in cm^{-1}) of the exchange Hamiltonian (9) computed for two Sc atoms separated by a distance of $R_{ab} = 3.205$ Å

$(k_1k_2)k$	$\tilde{J}_0^{(k_1k_2)k}$	$(k_1k_2)k$	$\tilde{J}_0^{(k_1k_2)k}$
(00)0	288.89	(44)2	—228.35
(11)0	1138.65	(04)4	754.26
(22)0	1217.95	(13)4	—1485.54
(33)0	598.74	(22)4	1894.54
(44)0	48.52	(24)4	921.47
(02)2	—671.58	(33)4	226.28
(11)2	996.18	(44)4	755.88
(13)2	—1428.70	(24)6	—3449.97
(22)2	350.09	(33)6	2898.43
(24)2	—994.64	(44)6	—1915.43
(33)2	—297.13	(44)8	9557.23

ical harmonics are allowed to assume values k = 0, 2, ..., 8. The presence in the unfilled shells of only one electron per shell eliminates hybrid integrals and makes the existence of a number of terms of the parameters $J^{k_1k_2}_{q_1q_2}$ impossible, and this in turn leads to a considerable simplification of the exchange Hamiltonian (9): Of the entire expression for it only the terms with the constants $J_0^{(k_1k_2)k}$ remain.

The five overlap integrals $(2m_a|2m_b)$, the five exchange integrals $(2m_a|r^{-1}|2m_b)$ of the electron-nucleus interaction, the 19 exchange integrals $(2m_a 2m_b|r^{-1}|2m_b' 2m_a')$ of the electrostatic interaction between the electrons, and the 19 direct integrals of these interactions that enter into $J^{k_1k_2}_{q_1q_2}$ were computed by us exactly for the internuclear distance $R_{ab} = 6.056$ a.u. = 3.205 Å, using the radial functions of Sc atoms (configuration 3d 4s^2, term ^{2}D) represented in the form of a linear combination of five Gaussian exponential functions[22]. The same functions were used to compute all the kinetic-energy and intratomic electrostatic-interaction integrals necessary for the determination of the quantities Z. The effective charges themselves turned out to be equal to 6 and 17, the largest deviations from the mean values being equal to 0.18 and −0.24. The values found with these effective-charge values for the parameters $\tilde{J}_0^{(k_1k_2)k}$ of the Hamiltonian (9) in which the tensor operators V_q^k are replaced by the unit irreducible tensor operators $U_q^k = (2k+1)^{-1/2} V_q^k$, are presented in the Table. It can be seen from the Table that the Hamiltonian parameters characterizing the exchange anisotropy (the parameters $\tilde{J}$ with $k \neq 0$) have the same order of magnitude as the parameters of the isotropic Hamiltonian (the parameters with k = 0). And although the role of the anisotropic terms will be somewhat lessened by the tendency of the 3j symbols and the reduced matrix elements of the tensor operators to decrease as the ranks of the latter increase, the replacement of the entire Hamiltonian (9) by a Heisenberg-type operator would, nevertheless, have been an absolutely unjustified procedure.

3. THE CRYSTAL-FIELD-INDUCED EXCHANGE ANISOTROPY

To proceed further with the investigation of the exchange anisotropy, let us concretize even more the system under consideration by assuming that each of the interacting atoms is located in a crystal field with the symmetry group D_{3h}, i.e., let us consider a situation analogous to the one obtaining in metallic scandium. In a field with such a symmetry, the D term of the Sc atom splits up into three levels[23] with wave functions:

$$\Gamma_{h1}\Psi = |20\rangle;$$

$$\Gamma_{h5}\begin{cases}\Psi_1 = |21\rangle \\ \Psi_2 = -|2-1\rangle\end{cases}, \quad \Gamma_{h6}\begin{cases}\Psi_1 = |22\rangle \\ \Psi_2 = |2-2\rangle\end{cases}.$$

If we set the crystal-field parameters B_2^0 and B_4^0 equal to −7000 and −900 cm^{-1}, to which they are, according to our estimates, equal in the case of metallic Sc, then the orbital singlet turns out to be the lowest, and its functions with allowance for the spin-orbit coupling can be represented in the form

$$\Gamma_{h7}\begin{cases}\Psi_1 = M[|0\rangle^+ + \varepsilon|+1\rangle^-], \\ \Psi_2 = M[|0\rangle^- + \varepsilon|-1\rangle^+],\end{cases} \tag{10}$$

where only the magnitudes of the components of the angular momentum L = 2 along the hexagonal axis are conserved in the orbital states, the indices ± denote the spin functions $|{1/2} \pm {1/2}\rangle$, $M = (1+\epsilon^2)^{-1/2}$, and the degree ϵ of admixture of the states of the excited orbital doublet Γ_{h5} is approximately equal to 0.02.

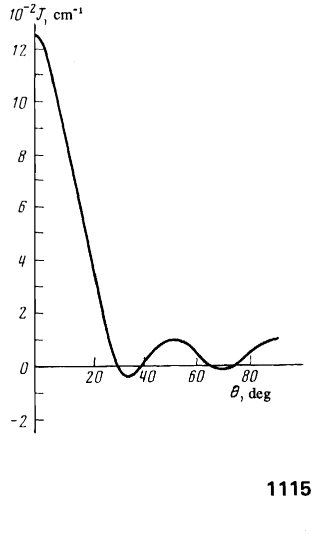
Because the Kramers doublet (10) is separated from the next excited level by an interval of the order of 5500 cm^{-1}, each of the interacting atoms can be characterized by an effective spin $\tilde{S} = 1/2$, and the exchange Hamiltonian can be written in terms of the effective spins quantized in the hexagonal axes in the form

$$\mathscr{H}_{\text{ex}} = J_\parallel \tilde{S}_1^z \tilde{S}_2^z + J_\perp (\tilde{S}_1^x \tilde{S}_2^x + \tilde{S}_1^y \tilde{S}_2^y). \tag{11}$$

The presence in the operator (9) of the spherical harmonics $C_q^k(\theta, \varphi)$ allows us now to easily follow the dependence of the effective-Hamiltonian parameters $J_\parallel$ and $J_\perp$ on the orientation of the pair axis with respect to the crystallographic axes. In order not to complicate the problem by investigating the relatively weak effect due to the angle φ, let us retain only the first terms in the wave functions (10). Computing the matrix elements of (9) with these functions, and comparing them with the elements of the Hamiltonian (11), we obtain for the parameters of the latter (in cm^{-1})

$$\begin{aligned} J_\parallel = J_\perp = J(\theta) = 89.82 + 198.61 C_0^2(\theta) + 309.95 C_0^4(\theta) \\ + 314.99 C_0^6(\theta) + 336.92 C_0^8(\theta). \end{aligned} \tag{12}$$

The quantity J determined by this expression as a function of the angle θ is shown in the figure, from which it can be seen that the exchange integral for the pair of atoms has its maximum value in the case when the pair is aligned along the hexagonal axis. Further, as the



Dependence of the exchange integral J, (12), on the angle θ of the direction of the pair with respect to the hexagonal axis.

angle θ is increased, the exchange integral begins to decrease rapidly, vanishing at approximately $\theta = 30°$ and subsequently assuming negative values. J may change its sign several times more in its subsequent variation with θ, remaining bounded in magnitude within a range of roughly 100 cm^{-1}. So strong a pair-axis-orientation dependence (of the magnitude and sign of the exchange integral) manifested by even a system in which the interacting atoms are in orbital singlet states will very likely turn out to be even more manifold for the cases of orbitally degenerate states.

4. THE EFFECTS OF THE SPIN-ORBIT COUPLING; THE MAGNETIC SUSCEPTIBILITY OF METALLIC SCANDIUM

Let us now take the admixed states into account in (10), and make an attempt to explain the anisotropy in the magnetic properties of metallic scandium. For this purpose, let us assume, in contrast to the point of view of investigators of the susceptibility of nonmagnetic metals[24], that the magnetism of the latter is due to localized d electrons. In such an approach, there immediately arises the question of the electron configuration of the atoms in the metal. In the scandium case under consideration, let us try to solve this problem by striving for an agreement between the theoretical magnetic moments for the directions along ($\mu_{\text{eff}}^{\parallel}$) and perpendicular ($\mu_{\text{eff}}^{\perp}$) to the hexagonal axis and their values extracted from the slopes of the temperature-dependence curves of the inverse paramagnetic susceptibilities.

If we use the most reliable experimental data[25], we find that $\mu_{\text{eff}}^{\parallel} \approx 1.73$, while $\mu_{\text{eff}}^{\perp} \approx 1.79$, and that these quantities remain constant right up to 5°K. The analysis carried out by us, including the consideration of the states of the configurations $3d^2$, $3d^2 4s$, and $3d^1$ in the presence of strong or intermediate crystal fields, showed that the only variant that allows the constancy of, as well as the above-indicated values for, the effective magnetic moments to be accounted for is the configuration $3d^1$ in a strong crystal field when each of the Sc atoms is described by the wave functions of the Kramers doublet (10) with the admixture factor ϵ lying within the interval 0.03—0.01, which agrees with the theoretical estimate of 0.02 for it.

The anisotropy of the paramagnetic susceptibility of a substance obeying the Curie-Weiss law is, besides the dependence of the effective magnetic moments on the direction of the applied magnetic field, also due to the anisotropy of the paramagnetic Curie temperatures. The latter can, in its turn, arise as a result of the crystal-field effects (one-particle anisotropy) and the exchange anisotropy (two-particle anisotropy). In the case (under consideration here) of atoms described by effective spins $\tilde{S} = 1/2$, the one-particle anisotropy is absent, and the entire effect has a two-particle character.

Let us assume that the effective magnetic field acting on each Sc atom in the hexagonal close-packed lattice is produced by twelve neighbors, six of which, at a distance of $R_{ab}^1 = 3.306$ Å, and located in the plane of the chosen atom, while the remaining six, at a distance of $R_{ab}^2 = 3.254$ Å, are located in the neighboring planes, each of these planes containing three of the atoms. Repeating the molecular-field-theory derivation with a Hamiltonian of the form (11) for each pair of interacting atoms, we obtain for the paramagnetic Curie temperatures measured in fields parallel and perpendicular to the hexagonal axis the expressions

$$\Theta_{\parallel} = -\frac{1}{4k}(6J_{\parallel}^1 + 6J_{\parallel}^2), \quad \Theta_{\perp} = -\frac{1}{4k}(6J_{\perp}^1 + 6J_{\perp}^2), \tag{13}$$

where k is the Boltzmann constant, while J^1 and J^2 are the parameters of the exchange Hamiltonian (11) for pairs with interatomic distances of R_{ab}^1 and R_{ab}^2 respectively.

Further, bearing in mind that for the first type of pairs the angle $\theta_1 = 90°$, while for the second $\theta_2 = 35°55'$, and assuming that all the two-center integrals for both types of pairs are the same and are equal to the values obtained by us in the earlier computations, we have for the magnitude of the anisotropy $\Delta\Theta = \Theta_{\parallel} - \Theta_{\perp}$ of the paramagnetic Curie temperature the expression (in degrees Kelvin)

$$\Delta\Theta = 930.75\varepsilon^4(1+\varepsilon^2)^{-2}.$$

It follows from the proportionality of $\Delta\Theta$ to the fourth power of the admixture factor ϵ that the value $\Delta\Theta = 65°\text{K}$ observed in[25] cannot be explained with any reasonable values of ϵ, even though the theoretical and experimental values for $\Delta\Theta$ have one and the same sign. At the same time, the values obtained for $\Theta_{\parallel}$ and $\Theta_{\perp}$ themselves in computations carried out under the same assumptions with $\epsilon = 0.02$ turn out to be equal to $-642°\text{K}$, which, for such a crude model, agrees quite well both in sign and in magnitude with the experimental values $\Theta_{\parallel} = -1000°\text{K}$, $\Theta_{\perp} = -1165°\text{K}$. These facts possibly indicate that the direct exchange interaction plays an important role in the explanation of the paramagnetic susceptibility of metallic scandium, whereas the anisotropy Θ is, apparently, due to some other causes.

At the same time, we must point out that an anisotropy Θ of the requisite sign and magnitude can be accounted for on the basis of a direct exchange. For this purpose, however, it is necessary to repudiate the ideality of the crystal lattice, and assume that at least one of the twelve pairs considered above does not participate in the production of the effective magnetic field, i.e., that at least one of the twelve nearest-neighbor Sc atoms has been replaced by some other particle. The quantity $\Delta\Theta$ then becomes proportional to the first power of ϵ, and begins to depend on the purity of the samples in question. It will probably make sense to undertake a more detailed investigation on this account only when the corresponding experimental data become available.

In conclusion, let us note that the operator form (9) of the exchange Hamiltonian remains unchanged when allowance is made for the indirect coupling of the ions through the conduction electrons. Only additional contributions to the parameters $J_0^{(k_1 k_2)k}$ arise when this allowance is made. It follows from this that the majority of the results obtained here will remain qualitatively valid in the more realistic model for a metal. In particular, in the case of an orbital singlet there will exist, as before, a "latent" exchange anisotropy that is capable, when the pair orientation relative to the crystallographic axes is varied, of leading to the alternation of the sign of the parameter J of the Heisenberg Hamiltonian.

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235