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[1]C. B. Duke and C. W. Tucker, Jr., Phys. Rev. Lett. 23, 1163 (1969); Surface Sci. 15, 231 (1969). For discussion of structure analyses within the spirit of the s-wave model see C. W. Tucker, Jr., and C. B. Duke, Surface Sci. 23, 411 (1970), and 24, 31 (1971); C. B. Duke and G. E. Laramore, Phys. Rev. B 2, 4765, 4783 (1970).

[2]C. B. Duke, J. R. Anderson, and C. W. Tucker, Jr., Surface Sci. 19, 117 (1970).

[3]R. O. Jones and J. A. Strozier, Jr., Phys. Rev. Lett. 22, 1186 (1969); J. A. Strozier, Jr., and R. O. Jones, Phys. Rev. Lett. 25, 516 (1970).

[4]J. B. Pendry, J. Phys. C: Proc. Phys. Soc., London 2, 1215, 2273, 2283 (1969).

[5]G. Capart, "Dynamical Calculations of LEED Intensities at Clear Copper (001) Surface (to be published).

[6]R. M. Stern and F. Balibar, Phys. Rev. Lett. 25, 1338 (1970).

[7]V. Hoffstein and D. S. Boudreaux, Phys. Rev. Lett. 25, 512 (1970).

[8]K. Kambe, Surface Sci. 20, 213 (1970).

[9]P. J. Jennings and E. G. McRae, Surface Sci. 23, 363 (1970).

[10]F. Jona, IBM J. Res. Develop. 14, 444 (1970).

[11]B. I. Lundqvist, Phys. Status Solidi 32, 273 (1969).

[12]J. I. Gersten, Phys. Rev. B 2, 3457 (1970).

[13]Duke and Laramore, Ref. 1.

[14]All energy scales quoted are measured with respect to the vacuum level, unless otherwise specified.

[15]Our definition of λ $(=k_2^{-1})$ is the same as that defined in Ref. 2 and is twice that defined in the first paper of Ref. 1.

[16]J. L. Beeby, J. Phys. C: Proc. Phys. Soc., London 1, 82 (1968).

[17]B. W. Holland and R. W. Hannum, to be published.

[18]J. B. Pendry, private communication.

[19]J. W. D. Connolly, in *Proceedings of the Symposium on Atomic, Molecular, and Solid-State Theory and Quantum Biology*, edited by P. Löwdin (Interscience, New York, 1969), p. 807.

[20]S. Y. Tong and T. N. Rhodin, to be published.

[21]M. G. Lagally and M. B. Webb, Phys. Rev. Lett. 21, 1388 (1968).

[22]E. G. McRae, J. Chem. Phys. 45, 3258 (1966).

Simple Theory of the Magnetic Properties of Rare-Earth Metals

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A simple theory for the magnetism of the rare-earth metals is presented. It is based on assuming strongly correlated, well-defined f-electron states of an atomiclike character which are weakly hybridized with conduction-band states. This hybridization plays the role of an indirect exchange interaction. A model calculation is presented: It yields for various values of the two relevant parameters ferromagnetic, antiferromagnetic, and helical arrangements. These arrangements are strongly dependent on the features of the conduction-electron band structure (Fermi surface). Order of magnitude estimates give reasonable agreement for physical parameters as determined from unrelated experiments.

We report here a simple theoretical model which explains qualitatively the many possible magnetic arrangements of the rare-earth metals.[1] In this model the usual roles of hybridization between f-like and conduction-band wave functions and correlation effects between f-like electrons are reversed, i.e., the correlation effects are taken into account as the important, zeroth-order contribution to the energy and the f-state–conduction-band hybridization terms are included as a perturbation.

The same zeroth-order Hamiltonian has been used successfully[2] to explain the α-γ phase transition in cerium metal. It assumes that the f levels and the conduction band are not hybridized. The conduction states are essentially noninteracting Bloch states derived from the $6s$ and $5d$ states of the atom. The localized f states are atomiclike (or ioniclike to be more precise) in character and are strongly correlated to one another, constituting on the whole a well-defined many-electron structure with well-defined total angular momentum J. The energetics of this structure is such that, for all phenomena involved here, only one electron can be either removed from an f shell and placed (really or virtually) in a conduction state or vice versa. If, for the sake of definiteness and simplicity, we assume that only occupations with zero or one f electron are permitted, or zero or one f hole as well, corresponding to cerium and ytterbium, respectively, then the f-electron system is represented in second quantization by

$$\mathcal{H}_f = \sum_i \sum_{m=-J}^{J} E a_{im}^{\dagger} a_{im}, \tag{1}$$

where E is the one-electron energy eigenvalue, i designates the ion site, and m is the magnetic quantum number. Correlation, which is the strongest effect in this case, imposes the constraint that no two states with the same i can be occupied simultaneously. The conduction-band electrons are represented by a term

$$\mathcal{H}_c = \sum_{k\sigma} \epsilon_k c_{k\sigma}^{\dagger} c_{k\sigma}, \tag{2}$$

as usual, and no constraint exists in this case.

When hybridization is taken into account, a new term in the Hamiltonian must be considered. It is of the form

$$\mathcal{H}_{\text{hyb}} = \sum_{k\sigma i m} [V_{k\sigma i m} c_{k\sigma}^{\dagger} a_{im} + V_{k\sigma i m}^{*} a_{im}^{\dagger} c_{k\sigma}]. \tag{3}$$

This term, among other effects, correlates in fourth order the magnetic moments of the f electrons at various sites and provides an interaction which gives rise to long-range magnetic ordering.

In order to show how the model allows for a large variety of magnetic arrangements, we have considered some very simple examples. In one such example we chose $J=\frac{1}{2}$, $m=\pm\frac{1}{2}$,

$$\epsilon_k = -W \cos(k_x a/2)\cos(k_y a/2)\cos(k_z a/2). \tag{4}$$

We have taken the Fermi energy ϵ_F to be a changing parameter

$$-W < \epsilon_F < W,$$

and the energy of the f level E to be

$$E < \epsilon_F,$$

but otherwise also free to vary. The hybridization matrix element was chosen to be

$$V_{\vec{k}\sigma i m} = \delta_{\sigma m} N^{-1/2} V_0 \exp(-i\vec{k}\cdot\vec{R}_i), \tag{5}$$

which is consistent with the completely periodic properties of the system and the neglect of spin-orbit coupling in the model; in (5) N is the number of ions in the crystal and V_0 has dimensions of energy.

The dispersion relation (4) corresponds to an s-like tight-binding band in a body-centered-cubic structure. The fourth-order perturbation correction of the hybridization Hamiltonian (3) can be easily expressed in the form of a Heisenberg Hamiltonian:

$$U = \sum_{i\neq j} \mathcal{J}(\vec{R}_i - \vec{R}_j)\vec{S}_i \cdot \vec{S}_j. \tag{6}$$

The results for $\mathcal{J}$ corresponding to the first three sets of nearest neighbors, $(\frac{1}{2}a, \frac{1}{2}a, \frac{1}{2}a)$, $(a, 0, 0)$, and $(a, a, 0)$, are shown in Table I for various values of $e_F \equiv \epsilon_F/W$ and $\Delta e = (\epsilon_F - E)/W$; $\mathcal{J}$ is expressed in units of

$$\mathcal{J}_0 \equiv 8\pi^{-6} V_0^4 W^{-3}. \tag{7}$$

A positive value indicates antiferromagnetic coupling and a negative $\mathcal{J}$ corresponds to a ferromagnetic interaction. The general trend of the values is such that (a) ferromagnetic interactions tend to appear for ϵ_F close to either the top or the bottom of the conduction band; and (b) antiferromagnetic coupling is preponderant for ϵ_F close to 0, i.e., in the middle of the band.

With the interaction (6) and the values of Table I we have calculated *classically* the spin arrangement which minimizes the total energy. The minimum energy arrangements are, except for an arbitrary uniform rotation of all spins, of the form

$$\vec{S}(\vec{R}_i) \equiv S(\sin\theta_i, 0, \cos\theta_i), \tag{8}$$

where

$$\theta_i = \vec{g}\cdot\vec{R}_i \tag{9}$$

and

$$\vec{g} = (2\Delta\theta/a)(0, 0, 1). \tag{10}$$

Table I. Magnetic arrangement for various configurations of a simple model.

e_F	Δe	$\mathcal{J}/\mathcal{J}_0$ {111}	$\mathcal{J}/\mathcal{J}_0$ {200}	$\mathcal{J}/\mathcal{J}_0$ {220}	$\Delta\theta$
0.97	0.05	-521	-351	-198	0
0.97	0.25	-30	-21	-12	0
0.75	0.05	-598	113	422	2/5 π
0.75	0.25	-151	-55	13	0
0.50	0.05	2,306	2,578	482	27/40 π
0.50	0.25	64	209	68	22/40 π
0.50	1.00	-5	15	7	19/40 π
0.25	0.05	15,512	4,584	-2,936	π
0.25	0.25	532	411	-129	π
0.00	0.05	6,013	-38,300	-268	π
0.00	0.25	651	-2,690	-28	π
-0.10	0.05	-1,890	7,780	-269	2/5 π
-0.10	0.15	145	1,210	-51	11/20 π
-0.10	0.40	143	116	-12	π
-0.25	0.05	-9,100	3,080	807	0
-0.25	0.25	-430	580	8	1/4 π
-0.25	0.50	-72	195	-3	3/8 π
-0.50	0.05	-5,390	-2,150	450	0
-0.50	0.50	-120	4	27	0
-0.50	0.75	-51	8	13	1/5 π
-0.75	0.05	-5,080	-2,930	-2,270	0
-0.75	0.25	-294	-174	-74	0
-0.97	0.05	-174	223	-380	0
-0.97	0.25	-19	6	-24	0

Values of $\Delta\theta$ are given also in Table I. A value of $\Delta\theta = 0$ corresponds to a complete ferromagnetic arrangement, $\Delta\theta = \pi$ is a perfect antiferromagnet, and an arbitrary $\Delta\theta$ gives a helical arrangement with a pitch $p = a\pi/2\Delta\theta$. It can be seen that a large variety of arrangements appears.

Several points are worth remarking:

(A) If in (2) ϵ_k is taken to be a free-electron dispersion relation proportional to k^2, $\mathcal{J}$ can be proven to give a "Ruderman-Kittel" type of coupling[3]

$$\mathcal{J}(\vec{R}) = \frac{2}{\pi} \frac{|\Delta|^2 \epsilon_F}{(\epsilon_F - E)^2} \frac{\cos 2k_F R}{(2k_F R)^3} + O((k_F R)^{-4}), \qquad (11)$$

where

$$|\Delta| = \pi \rho_F V_0^2 N^{-1} \qquad (12)$$

and ρ_F is the density of states at the Fermi level.

(B) Equations (11) and (12) are of the right order of magnitude. If we use Coqblin and Blandin's values,[4]

$$|\Delta| \cong 0.05 \text{ eV}, \quad \epsilon_F - E_0 \lesseqqgtr 0.1 \text{ eV},$$

corresponding to cerium, de Gennes's parameter[3,5] Γ (which is proportional to $\mathcal{J}$) turns out to be

$$\Gamma \approx 5.8 \text{ eV Å}^3,$$

while de Gennes estimates it from experiment to be

$$\Gamma \approx 5.7 \text{ eV Å}^3.$$

(C) As expected from general considerations[6] and from analogy to Cr metal,[7] the details of the Fermi surface are paramount in determining magnetic arrangements. In particular a perfectly "nesting" Fermi surface, such as in our example for $\epsilon_F = 0$, should strongly favor a perfect antiferromagnetic ordering.

(D) It should be emphasized however that the mechanism responsible for magnetic properties in our theory is different from either the "Ruderman-Kittel" contact interaction[3,5] or the extended itinerant electron-exchange mechanism[8] responsible for the spin-density wave state of chromium. The exchange in this case is perfectly localized and restricted to f-electron–f-electron interaction in the same ionic site; it is in this sense a strongly repulsive "hard-core" interaction. The long-range coupling between spins is a one-electron effect, i.e., a small hybridization of the f shell and the conduction states caused by the lattice potential. The conduction-electron dispersion relation, which defines the "polarizability" of the medium, plays in this case (as in all the other analogous ones) the role of propagating to the spin-spin interactions the singularities due to the Fermi distribution.

(E) In our formulation the effect appears in fourth-order perturbation theory because two spins have to flip to interact with one another, and each spin flip involves as usual two scattering processes ("in" and "out" or vice versa) between extended and localized states.

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[1]K. N. R. Taylor, Contemp. Phys. 11, 423 (1970).

[2]R. Ramirez and L. M. Falicov, Phys. Rev. B (to be published).

[3]M. A. Ruderman and C. Kittel, Phys. Rev. 96, 99 (1954); C. Kittel, *Quantum Theory of Solids* (Wiley, New York, 1963), and in *Solid State Physics*, edited by H. Ehrenreich, F. Seitz, and D. Turnbull (Academic, New York, 1969), Vol. 22, p. 1.

[4]B. Coqblin and A. Blandin, Adv. Phys. 17, 281 (1968).

[5]P. G. de Gennes, J. Phys. Radium 23, 510 (1962).

[6]O. K. Anderson and T. L. Loucks, Phys. Rev. 167, 551 (1968).

[7]J. C. Kimball, Phys. Rev. 183, 533 (1969), and many references cited therein.

[8]C. Herring, in *Magnetism*, edited by G. T. Rado and H. Suhl (Academic, New York, 1966), Vol. 4.

ic, New York, 1966), Vol. 4.