For the thorium–rare-earth alloys there is no resistivity minimum of the type discussed by Kondo and there are no irregularities which might be associated with a Néel temperature.[15,16] This seems to indicate a very weak spin coupling between the impurities and the conduction electrons. To corroborate this conclusion we have measured the depression of the superconducting transition temperature, T_c, by the addition of Gd. A preliminary measurement gives 3°K/at.%, a value much smaller than that found for the transition metals Mn and Cr in Zn,[17] but still comparable to La-Gd.[18] Only the exchange part of the scattering makes a major contribution to the depression of T_c,[19] so this result supports the weak-spin-coupling conclusion.

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"Muffin-Tin" Potential in Band Calculations*

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A prescription is given for defining a potential for use in augmented-plane-wave and Green's-function band calculations.

IN the augmented-plane-wave[1] and Green's-function[2] methods for solving the Schrödinger equation in a regular lattice it is usual to divide a cell of the crystal into two regions, one in which the potential is spherically symmetric and the other in which it is constant. This is indicated schematically in Fig. 1 where the two regions are labeled S and R. This "muffin-tin" potential is obtained by assuming a potential $V(\mathbf{r})$ which has a more complicated spatial form and averaging it, in S over angles and in R over the volume.[3]

We want to suggest here an alternative procedure which seems to us to be particularly appropriate when a self-consistent field band calculation is done.

The starting point is the expression for the total energy in the Hartree-Fock approximation:

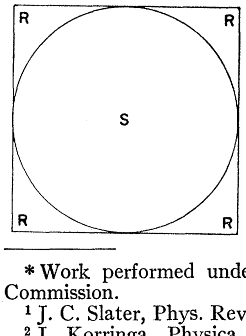

FIG. 1. Schematic diagram of a cell in a crystal lattice. The charge density is assumed to be approximately spherically symmetric in S and approximately constant in R.

$$\mathcal{E}=\sum_i (i|-\tfrac{1}{2}\nabla^2-Z/r|i)+\tfrac{1}{2}\sum_{ij}[(ij|1/r_{12}|ij) - (ij|1/r_{12}|ji)]. \quad (1)$$

(Atomic units are used, and we confine ourselves to a single cell of the crystal with appropriate boundary conditions on the one-electron wave functions.) For the exchange energy we substitute the statistical approximation[4];

$$-\frac{1}{4\pi^3}\int [3\pi^2\rho(\mathbf{r})]^{4/3}d\mathbf{r}, \quad (2)$$

where, of course, $\rho(\mathbf{r})=\sum_i|\varphi_i(\mathbf{r})|^2$. In terms of the charge density $\rho(\mathbf{r})$ the direct part of the potential energy is

$$-Z\int \rho(\mathbf{r})/r d\mathbf{r}+\tfrac{1}{2}\int\int \rho(\mathbf{r})\rho(\mathbf{r}')/|\mathbf{r}-\mathbf{r}'|d\mathbf{r}\, d\mathbf{r}'. \quad (3)$$

The integrals in Eqs. (2) and (3) are now broken up into integrals over the regions R and S. For example,

$$\tfrac{1}{2}\int\int \rho(\mathbf{r})\rho(\mathbf{r}')/|\mathbf{r}-\mathbf{r}'|d\mathbf{r}d\mathbf{r}'=\tfrac{1}{2}\int_{\mathrm{R}} d\mathbf{r}\,\rho(\mathbf{r})\int_{\mathrm{R}} d\mathbf{r}' \times\rho(\mathbf{r}')/|\mathbf{r}-\mathbf{r}'|+\int_{\mathrm{R}} d\mathbf{r}\,\rho(\mathbf{r})\int_{\mathrm{S}} d\mathbf{r}'\,\rho(\mathbf{r}')/|\mathbf{r}-\mathbf{r}'| +\tfrac{1}{2}\int_{\mathrm{S}} d\mathbf{r}\,\rho(\mathbf{r})\int_{\mathrm{S}} d\mathbf{r}\,\rho(\mathbf{r}')/|\mathbf{r}-\mathbf{r}'|. \quad (4)$$

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We now assume that the *charge density* is close enough to being spherically symmetric in S for it to be replaced by its spherical average

$$\rho(r)=\frac{1}{4\pi}\int \rho(\mathbf{r})\,\sin\theta d\theta\, d\varphi,$$

in integrals over the region S, and is close enough to a constant in R for it to be replaced by a volume average

$$\int_{\mathrm{R}}\rho(\mathbf{r})d\mathbf{r}\Big/\int_{\mathrm{R}}d\mathbf{r}$$

in integrals over the region R.

We thus arrive at new approximate expressions for the various integrals involved in the direct and exchange potential energies. For example the second integral on the right-hand side of (4) becomes

$$\langle 1/r\rangle_{\mathrm{R}}\int_{\mathrm{R}}\rho(\mathbf{r})d\mathbf{r}\int_{\mathrm{S}}\rho(r')d\mathbf{r}',$$

where

$$\langle 1/r\rangle_{\mathrm{R}}=\int_{\mathrm{R}}(1/r)d\mathbf{r}/\Omega_{\mathrm{R}},$$

and Ω_{R} is the volume of the region R.

With these new expressions for the direct and exchange potential energies, a new approximate expression for the total energy is formed. It is

$$\begin{aligned}\mathcal{E}=&-\tfrac{1}{2}\sum_i\int_{\mathrm{R+S}}\varphi_i^*\nabla^2\varphi_i d\mathbf{r}-Z\int_{\mathrm{S}}\rho/r d\mathbf{r}-Z\langle 1/r\rangle_{\mathrm{R}}\int_{\mathrm{R}}\rho d\mathbf{r}\\&+\tfrac{1}{2}\int_{\mathrm{S}}\int_{\mathrm{S}}\rho(r)\rho(r')/|\mathbf{r}-\mathbf{r}'|\,d\mathbf{r}\,d\mathbf{r}'+\langle 1/r\rangle_{\mathrm{R}}\int_{\mathrm{R}}\rho(\mathbf{r})d\mathbf{r}\\&\times\int_{\mathrm{S}}\rho(r')d\mathbf{r}'+\tfrac{1}{2}\langle 1/r_{12}\rangle_{\mathrm{RR}}\left[\int_{\mathrm{R}}\rho d\mathbf{r}\right]^2\\&-\frac{1}{4\pi^3}\int_{\mathrm{S}}[3\pi^2\rho(r)]^{4/3}d\mathbf{r}-\frac{1}{4\pi^3}\Omega_{\mathrm{R}}\left[3\pi^2\int_{\mathrm{R}}\rho d\mathbf{r}/\Omega_{\mathrm{R}}\right]^{4/3},\end{aligned}\quad(5)$$

where

$$\langle 1/r_{12}\rangle_{\mathrm{RR}}=\int_{\mathrm{R}}\int_{\mathrm{R}}1/|\mathbf{r}-\mathbf{r}'|\,d\mathbf{r}\,d\mathbf{r}'/\Omega_{\mathrm{R}}^2.$$

Keeping in mind that $\rho(\mathbf{r})=\sum_i|\varphi_i(\mathbf{r})|^2$, the φ_i's are varied to find the stationary values of the total energy. The following self-consistent field equations are then obtained:

$$\begin{aligned}&\Big[-\tfrac{1}{2}\nabla^2-Z/r+\int_{\mathrm{S}}\rho(r')/|\mathbf{r}-\mathbf{r}'|\,d\mathbf{r}'+Q_{\mathrm{R}}\langle 1/r\rangle_{\mathrm{R}}\\&\qquad-(3\pi^2\rho(r))^{1/3}/\pi-E_i\Big]\varphi_i(\mathbf{r})=0,\quad \mathbf{r}\text{ in S}\\&\Big[-\tfrac{1}{2}\nabla^2-(Z-Q_{\mathrm{S}})\langle 1/r\rangle_{\mathrm{R}}+Q_{\mathrm{R}}\langle 1/r_{12}\rangle_{\mathrm{RR}}\\&\qquad-(3\pi^2Q_{\mathrm{R}}/\Omega_{\mathrm{R}})^{1/3}/\pi-E_i\Big]\varphi_i(\mathbf{r})=0,\quad \mathbf{r}\text{ in R}.\end{aligned}\quad(6)$$

In Eq. (6) Q_{R} and Q_{S} are total electronic charges in R and S, and the other symbols have already been defined. Continuity of $\varphi_i(\mathbf{r})$ and $\nabla\varphi_i(\mathbf{r})$ is required at the boundary between R and S. The equations (6) are our main result. They define the required muffin-tin potential.

The exchange part of the potential in Eqs. (6) is $\frac{2}{3}$ of the magnitude of that proposed by Slater.[5] This smaller exchange potential has given good results in recent *atomic* calculations,[6] but no clear evidence exists as yet as to what is the best exchange potential to use for band calculations or, indeed, if there is a single best one for all purposes.[7]

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