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# EXCHANGE INTEGRAL IN RARE-EARTH METALS

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Calculations of 4*f*-6*s* electron exchange integrals have been made in order to determine the sign of the exchange integral and the dependence of the integral upon interatomic distance. The exchange integral is found to be positive in sign, and insensitive to changes of interatomic distance. By contrast, the magnetic interactions in rare-earth metals are quite sensitive to changes of interatomic distances in the crystal; it is concluded that this sensitivity is not attributable to variations of the exchange integral.

Two questions which are of interest in the theory of magnetic and electronic interactions in the rare-earth metals are as follows: (1) What is the sign of the 4*f*-electron–conduction-electron exchange integral $I(k,k')$? (2) What is the dependence of $I(k,k')$ upon interatomic distance? The first question is discussed in detail by Van de Braak and Caspers[1]; the second is of interest in the interpretation of the effect of pressure upon the Curie temperatures of the rare-earth metals.[2-4]

A problem which arises in a calculation of $I(k,k')$ is that accurate wave functions for the conduction electron are not available. One approximation has recently been made by Van de Braak and Caspers[1] who evaluated $I(k,k')$ for the case when the conduction electron is represented by a plane wave in an *s* state. They found $I(k,k')$ to be positive; their $I(k,k')$ is insensitive to interatomic distance.

Elliott[5] has suggested that "$I(k,k')$ will be similar to the atomic 6*s*-4*f* exchange integrals. It will probably not depend very strongly on *k* and *k*′." Based upon this suggestion we have calculated upon the 7094 computer the exchange integral *I* for gadolinium, using a 6*s* wave function to represent the conduction electron instead of the plane-wave approximation. It appears quite reasonable to assume that where the 4*f* wave function is large, i.e., in the inner regions of the electronic structure of the ion, the conduction electron is expected to possess some of the characteristics of a bound 6*s* electron.

The general expression for a 6*s*-4*f* exchange integral is

$$I=\iint\psi_{4f}^*(\vec{r}_1)\psi_{6s}^*(\vec{r}_2)\frac{e^2}{r_{12}}\times\psi_{4f}(\vec{r}_2)\psi_{6s}(\vec{r}_1)d\vec{r}_1d\vec{r}_2, \tag{1}$$

where each symbol has its usual meaning.

Substituting

$$\psi_{6s}(\vec{r})=R_{6s}(r)Y_0^{\,0}(\theta,\varphi), \tag{2}$$

$$\psi_{4f}(\vec{r})=R_{4f}(r)Y_{l'}^{\,m'}(\theta,\varphi), \tag{3}$$

and

$$\frac{1}{r_{12}}=\sum_{l,m}\frac{4\pi}{2l+1}\frac{r_<^{\,l}}{r_>^{\,l+1}}Y_l^{\,m}(\theta_1,\varphi_1)Y_l^{\,m*}(\theta_2,\varphi_2) \tag{4}$$

into Eq. (1), with $l'=3$ for a 4*f* electron, one finds that

$$I=\frac{e^2}{2l'+1}\int_0^\infty dr_2r_2^{\,2}R_{6s}(r_2)R_{4f}(r_2)\times\int_0^\infty dr_1r_1^{\,2}R_{6s}(r_1)R_{4f}(r_1)\frac{r_<^{\,3}}{r_>^{\,4}}. \tag{5}$$

Equation (5) was evaluated upon the computer. The radial wave functions used were those given by Freeman and Watson[6] based upon their Hartree-Fock calculations for a free ion. The 4*f* function for $\mathrm{Gd}^{+3}$ was given in the form

$$rR_{4f}(r)=\sum_{i=1}^{4}C_ir^4\exp(-Z_ir).$$

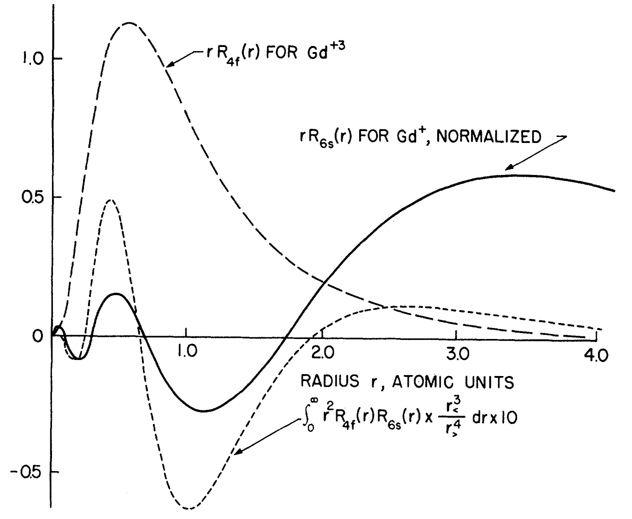

FIG. 1. Behavior of some atomic functions for gadolinium. $rR_{4f}(r)$ and $rR_{6s}(r)$ are from Freeman and Watson.

For 6*s* wave functions, the only data available were a graph for $Gd^+$, and this graph was scaled to obtain $rR_{6s}(r)$.

Figure 1 displays $rR_{4f}(r)$, $rR_{6s}(r)$, and the second integral in Eq. (5), viz.

$$\int_0^\infty dr_1 r_1^2 R_{6s}(r_1) R_{4f}(r_1) r_<^3/r_>^4.$$

As is seen, for the most part, the second integral is positive and negative, respectively, in the same regions that $rR_{6s}(r)$ is positive and negative. Thus, throughout almost the whole range of $r_2$, the product $R_{6s}(r_2)\int_0^\infty dr_1 r_1^2 R_{4f}(r_1) \times R_{6s}(r_1) r_<^3/r_>^4$ is positive; hence, the exchange integral $I$ is found to be positive.

As is expected, $I$ has its major contributions from the region where $rR_{4f}(r)$ is large, i.e., from the region within the core of the ion. The expected effect of pressure would be to modify the 6*s* wave functions primarily in the outer regions where $rR_{4f}(r)$ is small. To illustrate how little the outer part os the 6*s* wave function contributes to $I$, if $rR_{6s}$ is set identically equal to zero in the range $r \geq 1.7$ atomic units (a.u.) the value of $I$ only decreases by about 3%. Results are shown in Table I. For reference, the interatomic distance in Gd is about 6.8 a.u.

According to these results, $I$ is relatively insensitive to changes of interatomic distance such as are brought about by the application of pressure to the crystal. By contrast, magnetic transition temperatures in rare-earth metals are quite sensitve to pressure, and hence to interatomic spacings. For example, the Curie temperature of gadolinium is found to decrease by 10% with the application of 20 kbar pressure.[3] Evidently, changes in the transition temperatures are attributable to something other than the variation of the exchange integral. A more complete discussion of this point, together with new high-pressure data, is being prepared for a complete journal article.

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Table I. $10^{+2}e^{-2}(2l'+1)I$ (a.u.$^{-1}$) [see Eq. (5)] for some rare-earth metals.

| Gadolinium | Dysprosium | Erbium | Comment |
|---|---|---|---|
| 0.8188 | 0.7626 | 0.7108 | Wave functions in Fig. 1 |
| 0.091 89 | 0.076 41 | 0.059 | $rR_{6s}(r) = 0$ for $0 \leq r \leq 1.7$ |
| 0.8188 | 0.7626 | 0.7108 | $rR_{6s}(r) = 0$ for $0 \leq r \leq 0.1$ |
| 0.7915 | 0.7430 | 0.7001 | $rR_{6s}(r) = 0$ for $r \geq 1.7$ |
| 0.8078 | 0.7551 | 0.7062 | $rR_{6s}(r) = 0$ for $r \geq 3.4$ |