Additional Crystalline Electric Field Potentials for Heavy Rare Earth Metals

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A derivation is given of additional crystalline potential energy terms due to the interaction of conduction electrons with the localised electrons of ions in pure heavy rare earth metals. Explicit expressions for the $A_{4}^{4}$ and $A_{4}^{6}$ coefficients are given to supplement those of $A_{4}^{2}$ and $A_{6}^{6}$ given in a recent paper. Additional contributions which arise from the unfilled $f$ shells of the neighbours of any particular ion under consideration, are derived but shown to be of such a magnitude that, for most purposes, they can be neglected. The use of Slater orbitals in calculating enhancement factors for $A_{4}^{4}$ and $A_{6}^{6}$ is discussed with particular reference to those contributions which involve resonance amplitudes and mainly involve the $f$ orbitals.

I. Introduction

In the heavy rare earth metals crystalline electric field (CEF) potentials play a significant part in determining magnetic properties. There are three main contributions to the four necessary coefficients $A_{2}^{0}$, $A_{4}^{0}$, $A_{2}^{6}$ and $A_{6}^{6}$ for hexagonal symmetry. The potential energy of the electrons in the incomplete $f$ shell is perturbed by the presence of electric fields originating from all the metal ions in the crystal lattice. This has been studied in detail by Kasuya (1966), Das and Ray (1969) and De Wette and Nijboer (1958) and their studies show that crystal fields are much enhanced over those arising from nearest neighbours only. The effective crystal field potential in which a $4f$ electron moves is however decreased by the presence of the filled orbitals of each metal ion, Sternheimer et al. (1968). The third contribution, namely the enhancement due to conduction electrons, has recently been considered by Dixon and Dupree (1971, I and II) who examined in detail the $A_{2}^{2}$ and $A_{6}^{6}$ coefficients, the former being representative of the axial field and the latter the hexagonal component. They assumed that the conduction electrons did not interact strongly with themselves and that the conduction electron wavefunction was a plane wave orthogonalised to all the occupied orbitals of the rare earth's neighbours and all of its own occupied orbitals up to $5p$, $5s$, except one. This latter orbital $\psi_{e}$ was that $f$ orbital for which the probability of occupancy of an extra electron, added to those of the ground configuration, could be expected to be highest, due to its low energy.

Both $A_{2}^{2}$ and $A_{6}^{6}$ were found to be enhanced by a factor which was not strongly dependent on the orbital $\psi_{e}$ and arose from orthogonalising the conduction electron wavefunction $\psi_{e}$ to the occupied orbitals of the rare earth's twelve neighbours. On the other hand $A_{2}^{0}$ contained an extra factor $R_{1}$ which was entirely due to the orbital $\psi_{e}$ and hence to the fact that the central rare earth ion had an incomplete $f$ shell. It was therefore somewhat surprising to find that both the CEF parameters
were not enhanced by factors which arose from the unfilled f shells of nearest neighbors. That this is in fact the case is by no means clear nor is it immediately evident why such a contribution to, for example, the $A_{2g}^0$ parameter is small. The present paper attempts an understanding of these terms in the enhancement of CEF parameters by conduction electrons.

II. Outline of the Model

The model developed in I considered essentially the volume $V$ enclosed by the twelve nearest neighbors of a rare earth at the origin. In this volume it was supposed that there were $n_0$ conduction electrons which did not interact with each other. If the c-axis is taken as the z-axis, then the co-ordinates of the twelve rare earth ions are $(0, 0, 0)$, $(a, 0, 0)$, $(\pm a/2, \pm \sqrt{3}a/2, 0)$, $(0, a/\sqrt{3}, \pm b \cos \alpha)$ and $(\pm a/2, -a/\sqrt{3}, \pm b \cos \alpha)$ where $a$ is the nearest neighbor distance in the $xy$ plane and the metal ions above the plane are a distance $b$ from $(0, 0, 0)$ and subtend an angle $\alpha$ with the z-axis. The $z$-axis was taken as the polar axis of a system of spherical polar co-ordinates and each conduction electron was described by a wavefunction

$$\Psi_k = \frac{N}{\sqrt{V}} \{e^{i\mathbf{k} \cdot \mathbf{r}} - \sum a_\alpha (1 + \delta \varepsilon) \Psi_\alpha\}$$

where $N$ is a normalisation constant, $k$ is taken to be the Fermi wave vector, and $a_\alpha$ is the overlap of the wavefunction $\Psi_\alpha$ with $e^{i\mathbf{k} \cdot \mathbf{r}}$ defined by $\int e^{i\mathbf{k} \cdot \mathbf{r}} \Psi_\alpha^* d\mathbf{r}$. $\varepsilon$ is a resonance amplitude which is constant for any particular metal and $\delta$ is defined to be unity for the state $\Psi_\varepsilon$ and zero otherwise. The sum over $\alpha$ was over all the occupied orbitals of the rare earth at $(0, 0, 0)$ and its nearest neighbors including all 4f orbitals up to $\delta p$ and $5s$ but excluding $6s$. It was demonstrated in I, that for the heavy rare earths the additional potential energy of a localised f electron at $\mathbf{r}_i = (r_i, \theta_i, \varphi_i)$ could be written

$$\int \frac{\Psi_k^* \Psi_k}{|\mathbf{r} - \mathbf{r}_i|} e^{i\mathbf{q} \cdot \mathbf{r}} d^3 \mathbf{r}.$$  \hspace{1cm} (1)

The analysis was divided into a consideration of terms due to the nearest neighbors and secondly terms arising from the ion at the origin where the electron with radius vector $\mathbf{r}_i$ was located. In the former case $\Psi_\alpha = \Psi_\alpha(r - \mathbf{r}_i)$ where $\mathbf{r}_i$ is the position vector of a metal neighbour and to perform the integration in (1) it became necessary to change to a variable $\mathbf{r}' = \mathbf{r} - \mathbf{r}_i$. To a good approximation $|\mathbf{r}' - \mathbf{r}_i| < |\mathbf{r}_i|$ so the denominator of the integrand of (1) may be expanded as

$$\frac{1}{|\mathbf{r}' + \mathbf{r}_i - \mathbf{r}_i|} = \sum_{l,m} \frac{l - |m|!}{l + |m|!} \frac{|r' - r_i|^l}{r_i^{l+1}} P^{|m|}(\cos \theta_i) P^{|m|}(\cos \bar{\theta}) \exp i m (\bar{\varphi} - \varphi_i)$$

\hspace{1cm} (2)

where $\bar{\theta}$ and $\bar{\varphi}$ are the polar co-ordinates of $|\mathbf{r}' - \mathbf{r}_i|$. In the second case no change of variable was necessary so that we have

$$\frac{1}{|\mathbf{r} - \mathbf{r}_i|} = \sum_{l,m} \frac{l - |m|!}{l + |m|!} \frac{r_i^{l+1}}{r_i^{l+1}} P^{|m|}(\cos \theta_i) P^{|m|}(\cos \theta) \exp i m (\varphi - \varphi_i).$$  \hspace{1cm} (3)

The numerator of the integrand in (1) was then treated term by term.