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Charge screening and magnetic anisotropy in metallic rare-earth systems

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The calculation of magnetic anisotropy constants is performed beyond the point-charge model for a continuous charge-density distribution of screening conduction electrons. An important role of the nonuniform electron density, in particular, of the Friedel oscillations, in the formation of crystal field is demonstrated. Such effects can modify strongly the effective ion (impurity) charge and even change its sign. This enables one to justify the anion model, which is often used for discussing experimental data on hydrogen-containing systems. Possible applications to the pure rare-earth metals and $R\mathrm{Co}_5$ (R=rare earth) compounds are discussed. The deformation of magnetic structure near the interstitial positive muon owing to the strong local anisotropy, and the corresponding contribution to the dipole field at the muon are considered. [S0163-1829(98)03701-1]

The old problem of strong magnetic anisotropy in the rare-earth-based intermetallic systems,[1] which has a great practical importance, has been extensively investigated. Recently the anisotropy induced by interstitial hydrogen atoms[2,3] and positive muons[4] has been discussed.

It is accepted now that the main mechanism of magnetic anisotropy origin in the rare-earth systems is the crystal-field one. Estimations of the anisotropy constants are usually performed in the point-charge model. At the same time, this model leads frequently to difficulties and contradictions with experimental data. For example, the calculated anisotropy constant K_1 in $R\mathrm{Co}_5$ (R=rare earth) compounds turns out to be very large and have an incorrect sign.[5] Thus screening of the crystal field should play an important role. This screening is often taken into account by introducing the effective ion charge Q^*, which can differ considerably from the bare ion charge. In particular, the fitted charge of hydrogen ions for the $R\mathrm{Co}_2$-based systems turns out to be negative (the anion model[2,3]). A physical explanation of such situations is not simple. Shielding of crystal fields in ionic solids was treated in Ref. 6. Screening by conduction electrons, which form some localized levels near the rare-earth ion, was discussed in Ref. 5. However, these effects turn out to be insufficient for explaining experimental data.

In the present paper we perform calculations of magnetic anisotropy constants with account of continuous charge-density distribution in a metal. We shall demonstrate that the magnetic anisotropy is strongly influenced not only by the total charge induced by surrounding ions or impurity centers, but also by a concrete form of screening electron density, in particular, by the Friedel oscillations.

We consider the magnetic ion at the point $\mathbf{r}=0$ in the crystal field of the surrounding charges. The spherically symmetric potential V_{cf}, which is induced by a center at the point $\mathbf{r}=\mathbf{R}$ and originates from the point charge Q_0 and conduction electron charge density $Z(|\mathbf{r}-\mathbf{R}|)$, has the form

$$V_{\mathrm{cf}}(\mathbf{r})=\frac{Q_0+Q_{\mathrm{el}}(|\mathbf{r}-\mathbf{R}|)}{|\mathbf{r}-\mathbf{R}|}, \tag{1}$$

where

$$Q_{\mathrm{el}}(r)=4\pi\int_0^r \rho^2 d\rho Z(\rho) \tag{2}$$

is the conduction electron charge inside the sphere with the radius r, $Q'_{\mathrm{el}}(r)=4\pi r^2 Z(r)$, the system of units where the electron charge $e=-1$ is used. At large r complete screening takes place, so that $Q_{\mathrm{el}}(\infty)=-Q_0$.

The anisotropy constants are determined from the angle dependence of the energy of the magnetic ions in the crystal field

$$\delta\mathcal{E}_{\mathrm{cf}}=-K_1\cos^2\theta+\cdots . \tag{3}$$

First we discuss the point-charge model. The dependence (3) is calculated with the use of the expansion in r, which corresponds to the expansion in small radius of the f shell:

$$\frac{1}{|\mathbf{r}-\mathbf{R}|}=\frac{1}{R}\left[1+\frac{r}{R}\cos\tilde{\theta}+\frac{r^2}{2R^2}(3\cos^2\tilde{\theta}-1)+\cdots\right]. \tag{4}$$

Here $\tilde{\theta}$ is the angle between the vectors $\mathbf{R}$ and $\mathbf{r}$, which can be expressed in the spherical coordinate system of the crystal as

$$\cos\tilde{\theta}=\cos\theta\cos\theta_{\mathbf{R}}-\sin\theta\sin\theta_{\mathbf{R}}\cos(\phi-\phi_{\mathbf{R}}), \tag{5}$$

where $\theta_{\mathbf{R}}$ and $\phi_{\mathbf{R}}$ are the polar and azimuthal angles of the vector $\mathbf{R}$. Substituting Eq. (5) into Eq. (4) and picking out the term that is proportional to $\cos^2\theta$, one obtains for the point-charge contribution (cf. Refs. 7 and 3)

$$K_1^{\mathrm{pc}}=-3\Lambda\langle r_f^2\rangle\alpha_J J(J-1/2)Q_0e^2, \tag{6}$$

where $\langle r_f^2\rangle$ is the average square of the f-shell radius, J is the total angular momentum of rare-earth ions, α_J is the Stevens factor,

$$\Lambda=\sum_{\mathbf{R}}\frac{3\cos^2\theta_{\mathbf{R}}-1}{R^3}. \tag{7}$$

For the hcp lattice with the parameters c and a (pure rare-earth metals) we derive after summation over nearest-neighbor magnetic ions the standard result (see Ref. 5)

$$\Lambda=6a^{-3}\left(16\frac{y^2-2/3}{(4/3+y^2)^{5/2}}-1\right)\simeq 2.44a^{-3}(\sqrt{8/3}-y), \tag{8}$$

where $y=c/a\simeq 1.57-1.59$ for heavy rare earths.[9] The small geometrical factor $\sqrt{8/3}-y=1.633-y\sim 0.05$ occurs due to the fact that the contributions from the magnetic ions in the same plane and in neighbor planes have opposite signs and almost cancel each other.

For the $R\mathrm{Co}_5$ compounds, where $R=a/\sqrt{3}$ for six neighbor Co ions in the same plane and $R=\frac{1}{2}\sqrt{a^2+c^2}$ for six Co ions in the upper and lower planes, we have[5]

$$\Lambda=6a^{-3}\left(16\,\frac{2y^2-1}{(1+y^2)^{5/2}}-3^{3/2}\right)\simeq-\frac{23.4}{a^3}, \tag{9}$$

with $y=c/a\simeq 0.8, a\simeq 5$ Å. In this case the cancellation of contributions from different planes does not play a crucial role, so that the expression in the brackets is never small.

Consider the case where anisotropy is induced by random next-neighbor substitutional or interstitial impurities. For an impurity in the octahedral interstitial of the hcp lattice[10] we have $R=a/\sqrt{2}$, $\cos\theta_{\mathbf{R}}=1/\sqrt{3}$. Then $\Lambda=0$ for the ideal hcp lattice, and the impurity contribution to K_1 vanishes, as well as Eq. (8) (note that the situation is different in the hydrogen-containing $R\mathrm{Co}_2$ systems[3]). However, there occurs the local anisotropy term

$$\delta\mathcal{E}_{\rm cf}=-K_{1\rm loc}\cos^2\tilde{\theta}, \tag{10}$$

with

$$K^{\rm pc}_{1\rm loc}=12\sqrt{2}\langle r_f^2\rangle\alpha_J J(J-1/2)Q_0e^2/a^3. \tag{11}$$

Note that for the positive charges Q_0 the signs of $K_{1\rm loc}$ and K_1 coincide.

Now we treat the case of a continuous charge distribution of the screening conduction electrons. Similar to Eq. (4), the potential (1) can be also expanded at small r. Performing the expansion of the integral (2) in

$$|\mathbf{r}-\mathbf{R}|-R=-r\cos\tilde{\theta}+(r^2/2R)\sin^2\tilde{\theta}+\cdots$$

we obtain up to r^2

$$\begin{aligned}Q_{\rm el}(|\mathbf{r}-\mathbf{R}|)={}&Q_{\rm el}(R)-4\pi R^2Z(R)r\cos\tilde{\theta}+2\pi Rr^2\\&\times\{Z(R)+[Z(R)+RZ'(R)]\cos^2\tilde{\theta}\}.\end{aligned} \tag{12}$$

Taking into account the expansion (4) we have

$$\begin{aligned}\frac{Q_{\rm el}(|\mathbf{r}-\mathbf{R}|)}{|\mathbf{r}-\mathbf{R}|}={}&\frac{Q_{\rm el}(R)}{R}\left[1-\frac{r}{R}\cos\tilde{\theta}+\frac{r^2}{2R^2}(3\cos^2\tilde{\theta}-1)\right]\\&-2\pi[Z(R)(2rR\cos\tilde{\theta}-r^2\sin^2\tilde{\theta})\\&-RZ'(R)r^2\cos^2\tilde{\theta}].\end{aligned} \tag{13}$$

Then we derive

$$K_1/K_1^{\rm pc}=Q^*/Q_0 \tag{14}$$

with the effective charge

$$Q^*=Q_0+Q_{\rm el}(R)-\tfrac{4}{3}\pi R^3[Z(R)-RZ'(R)]. \tag{15}$$

Thus we have obtained the expression for the effective charge Q^*, which should be used for calculating the observable anisotropy constant K_1. We see that the ratio (14) depends explicitly, besides the total charge inside the sphere with the radius R, also on the charge density $Z(R)$ and the derivative $Z'(R)$. The latter quantity can be large provided that the rare-earth ion lies in the region where the charge density changes sharply. Note that for the constant charge density Z $[Z'(R)=0,\ Q_{\rm el}(R)=\frac{4}{3}\pi R^3Z]$ we have $K_1=K_1^{\rm pc}$ and screening is absent (this is connected with the fact that the charge in the sphere increases as R^3, but the quadrupole interaction decreases as R^{-3}).

To obtain the value of Q^*, one has to investigate the charge screening for a concrete electronic spectrum, which is, generally speaking, a very difficult task. We discuss the one-center screening problem within a simple model of free conduction electrons ($E=k^2/2$) in the impurity-induced rectangular potential well which has the width d and depth $E_0=k_0^2/2$.[8] This model enables one to calculate the charge distribution of screening conduction electrons in terms of the scattering phase shifts η_l. The value of k_0 should be determined for given k_F and d from the Friedel sum rule

$$Q_0=\frac{2}{\pi}\sum_{l=0}^{\infty}(2l+1)\eta_l(k_F). \tag{16}$$

The phase shifts are calculated as

$$\tan\eta_0(k)=\frac{kd\ j_1(kd)-\beta_0 j_0(kd)}{kd\ n_1(kd)-\beta_0 n_0(kd)},\quad \beta_0=\tilde{k}d\frac{j_1(\tilde{k}d)}{j_0(\tilde{k}d)}, \tag{17}$$

$$\tan\eta_{l>0}(k)=\frac{kd\ j_{l-1}(kd)-\beta_l j_l(kd)}{kd\ n_{l-1}(kd)-\beta_l n_l(kd)},$$

$$\beta_l=\tilde{k}d\frac{j_{l-1}(\tilde{k}d)}{j_l(\tilde{k}d)}, \tag{18}$$

where $j_l(x)$ and $n_l(x)$ are the spherical Bessel and Neumann functions, $\tilde{k}^2=k_0^2+k^2$. The disturbance of the charge density is given by

$$\delta Z(r)=-\int_0^\infty k\,dk\ \delta\rho(k,r). \tag{19}$$

For $r>d$ one obtains

$$\begin{aligned}\delta\rho(k,r)/\rho_0(k)=\sum_l(2l+1)\{&[n_l^2(kr)-j_l^2(kr)]\sin^2\eta_l\\&-j_l(kr)n_l(kr)\sin 2\eta_l\},\end{aligned} \tag{20}$$

with $\rho_0(k)=k/\pi^2$. For $r<d$, joining of the wave functions at the boundary of the potential well $r=d$ yields

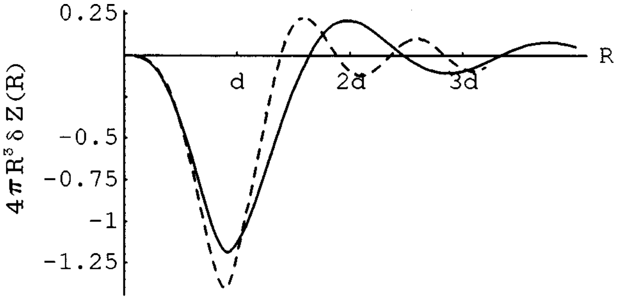

FIG. 1. The distance dependence of the function $4\pi R^3 \delta Z(R)$ for $k_F d=2$ (solid line) and $k_F d=3$ (dashed line).

$$\delta\rho(k,r)/\rho_0(k)=\sum_l (2l+1)[\,j_l(kd)\cos\eta_l - n_l(kd)\sin\eta_l]^2[\,j_l(\tilde{k}r)/j_l(\tilde{k}d)]^2-1. \tag{21}$$

The parameter d should be determined by the geometry of the lattice near the impurity. In Ref. 8, where impurities in the Ag host were considered, d was chosen to be equal to the Wigner-Seitz radius, so that $k_F d=2$. In the case where the impurity is localized in an interstitial the choice of d may be different.

We have performed the calculations for $k_F d=2$ and $k_F d=3$. At $Q_0=1$ Eq. (16) yields $k_0 d=1.46$ and $k_0 d=1.235$, respectively. With increasing k_F, the number of l values to be taken into account in the sums grows; for $k_F d=3$ the contributions up to $l=3$ are appreciable. The results are presented in Figs. 1–3. Note that a weak singularity occurs at the joining point $r=d$.

One can see that at $R<d$, except for the case of very small R where $Q^*(R)$ slightly decreases, the derivative term results in that $Q^*(R)$ grows [despite an increase of $|Q_{\mathrm{el}}(R)|$]. For $R\simeq d$, where Z' is maximum, the nonuniform distribution of electron density leads to the effective ion charge Q^* being positive and exceeding considerably its bare value Q_0 ($Q_0=1$ in our case). At the same time, with further increasing R the situation changes drastically: Z' decreases and becomes negative, so that ''overscreening'' of the ion charge occurs. Such a situation corresponds to the ''anion model.'' In the simple model under consideration, the values about -0.5 can be obtained for Q^* (the value of -1 was assumed for the hydrogen ions in Ref. 3). At large distances Q^* tends to zero, but considerable oscillations of the effective charge sign take place, which attenuate rather slowly. One can see from Fig. 2 that the contribution of the derivative term in Eq. (15) predominates at large R too. Of course, more complicated models are required for a regular lattice of screened charges, but the conclusion about an important role of the nonuniform distribution of electron charge should hold also in that case.

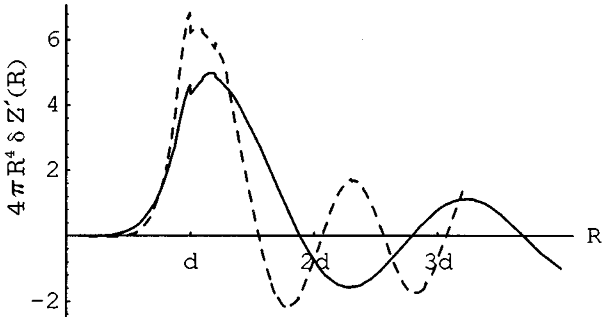

FIG. 2. The dependence $4\pi R^4 \delta Z'(R)$ for the same parameter values as in Fig. 1.

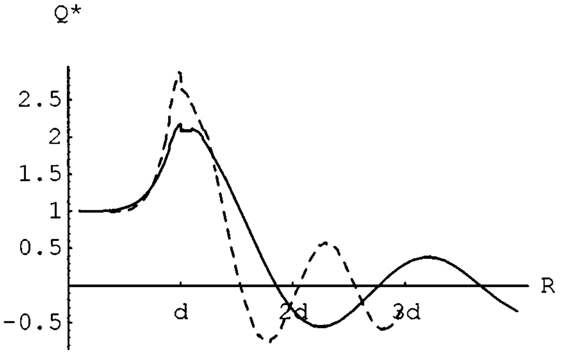

FIG. 3. The distance dependence of the effective charge $Q^*(R)$ for the same parameter values as in Fig. 1.

The effects of screening under consideration can be important for the values of the anisotropy constants in both stoichiometric rare-earth compounds and systems containing hydrogen and other impurities. The experimental data on the first magnetic anisotropy constant of the heavy rare-earth metals and corresponding $R\mathrm{Co}_{5+x}$ compounds at low temperatures are presented in Table I. The values of the effective charge Q^* are calculated by using Eqs. (14) and (6). One can see that the values of Q^* for the pure rare earths are of order of unity. At the same time, the effective charges of the Co ions in the $R\mathrm{Co}_{5+x}$ systems turn out to be negative and very small (a similar situation takes place in the case where R is a light rare earth[5]), so that a weak ''overscreening'' occurs. Note that in fact the effective charges may be different for

TABLE I. The total angular momenta J, Stevens factors α_J, average squares of the f-shell radius $\langle r_f^2\rangle$ (atomic units), and c/a ratios for rare-earth elements; the experimental values of K_1 (K/rare-earth ion) for the pure heavy rare earths (Ref. 1) and $R\mathrm{Co}_{5+x}$ systems [the contribution of rare-earth sublattice (Ref. 11)], and the corresponding calculated values of Q^*. The values of K_1^{exp} for Er and Tm are obtained from the anisotropy of magnetic susceptibility (see Ref. 12). The values of the local anisotropy constant $K_{1\mathrm{loc}}$ for an impurity in the octahedral interstitial of a rare-earth metal are calculated for $Q^*=1$.

R	Tb	Dy	Ho	Er	Tm
J	6	15/2	8	15/2	6
$\alpha_J\times 100$	-1.0	-0.63	-0.22	0.25	1.01
$\langle r_f^2\rangle$	0.76	0.73	0.69	0.67	0.64
c/a	1.58	1.57	1.57	1.57	1.57
K_1^{exp}	-123	-114	-50	58	100
Q^*	1.3	1.1	1.2	1.45	1
$K_{1\mathrm{loc}}^{\mathrm{calc}}/Q^*$	-2100	-2050	-800	800	2000
$R\mathrm{Co}_{5+x}$	$\mathrm{TbCo}_{5.1}$	$\mathrm{DyCo}_{5.2}$	$\mathrm{HoCo}_{5.5}$	ErCo_6	
K_1^{exp}	-96	-211	-203	80	
Q^*	-0.02	-0.03	-0.09	-0.04	

two kinds of the Co ions that contribute to Eq. (9), since the corresponding values of R are different. Besides that, a possible role of the neighbor rare-earth ions in the crystal field formation should be considered in such a situation.

Another interesting example is the case of imbedded positive muons,[10,13] which induce a strong local anisotropy. This leads to strong deformation of the magnetic structure near the muon and to a considerable contribution to the dipole field at the point of its location.[14,4] According to Table I, for $Q^* \sim 1$ the local anisotropy constants make up about 10^3 K and are large in comparison with the values of the molecular field acting on the rare-earth ions, $\lambda \sim 100$ K. Therefore a strong cast of magnetic moments should take place in the limit of large $K_{1\mathrm{loc}}$. In the case $K_1 > 0$, $K_{1\mathrm{loc}} > 0$ for the ferromagnetic ordering along the z axis we have for the dipole field

$$\Delta B^z_{\mathrm{dip}} = 4\sqrt{3} M/a^3 \sim 25 \text{ kG}, \tag{22}$$

where $M \simeq \sqrt{J(J+1)}\mu_B$ is the magnetic moment of rare-earth ion. In the case $K_1 < 0$, $K_{1\mathrm{loc}} < 0$ the direction and value of the dipole field depend on the relation between K_1 and λ (see Ref. 4), but $|\Delta \mathbf{B}_{\mathrm{dip}}|$ has the same order of magnitude. Thus the local distortion of the magnetic structure yields the contribution to $\Delta \mathbf{B}_{\mathrm{dip}}$, which is of the same order as the sum over the regular lattice (cf. the calculation for holmium;[15] note that the nearest-neighbor ions give zero contribution to this sum in the absence of the distortion). Phenomena that occur in ferromagnetic and helical phases at intermediate values of $K_{1\mathrm{loc}}$ with changing the relation between $K_{1\mathrm{loc}}$, K_1 and λ (e.g., with the change of temperature or external magnetic field) are discussed in Ref. 4.

To conclude, the effects of screening of ion (impurity) charge by conduction electrons turn out to be very strong: the anisotropy constants can be strongly modified and even change their signs. More quantitative investigations with account of a real electronic structure, multicenter effects and nonspherical charge-density distribution seem to be important for the problem of magnetic anisotropy in the systems under consideration.

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