

X-ray spin form factors of rare-earth ions

H. Adachi

Institute of Materials Structure Science, KEK, Tsukuba, Ibaraki 305, Japan

H. Miwa

Shinshu University, Matsumoto, Nagano 390, Japan

(Received 20 June 2002; published 31 December 2002)

The x-ray spin form factor obtained by the nonresonant magnetic diffraction where the magnetic moment in the target material is parallel to the scattering vector, being a unique microscopic approach to the aspherical density distribution of scatterers, has been theoretically investigated for the $4f$ electrons of the rare-earth ions. Examining the contribution from the lowest-order asphericity with the operator-equivalent technique, it is shown that the aspherical effect is relatively serious for the ions with small total-spin quantum numbers, such as Ce^{3+} , Pr^{3+} , Tm^{3+} , and Yb^{3+} , and it is illustrated that the relation of the expansion of the present *spin* form factor and the aspherical distortion of the $4f$ charge density along the moment direction is inverse between the less-than-half and more-than-half cases. It is also shown that, while the recent experiment on $SmAl_2$ appears to support the factorization of the relevant operators into the spatial and spin parts in calculating the thermal averages, the reliability of such a treatment could be tested by studying the thermal variation of the form factors for various rare earths or, if detectable, measuring the form factor of Eu^{3+} . It is emphasized through the paper that the x-ray magnetic diffraction of this specific geometry is a limited but hopeful way to study the spatial distribution of spin polarization in magnetic materials and could be complementary to the neutron-diffraction and Compton-scattering methods.

DOI: 10.1103/PhysRevB.66.224428

PACS number(s): 75.25.+z, 32.90.+a, 61.10.Dp, 78.70.Ck

I. INTRODUCTION

Nowadays, the diffraction study on the magnetism of condensed matters can be done by using both neutron and x rays. In particular, the number of research reports with the latter has been greatly increasing in the last two decades, due to the advent of synchrotron radiation. X rays having well-controlled polarization, such as synchrotron radiation, enable in theory the separation between the signals arising from the spin and orbital magnetic moments, since the x-ray scattering cross section associated with these two kinds of the magnetic moments are prefaced by different x-ray polarization factors.¹ So then, it is often said that the spin and orbital magnetization densities can be obtained independently with this technique. However, in almost all of the reports subsequent to the pioneering demonstration on the antiferromagnetic (helical magnetic) sample by Gibbs *et al.*² and that on the ferromagnetic (ferrimagnetic) sample by Collins *et al.*,³ this feature is utilized only in order to seek the absolute values of the atomic spin and orbital magnetic moments or the ratio of the two. That is to say, the form factor of each reflection obtained by the nonresonant magnetic diffraction is served for the extrapolation to the value at zero momentum transfer assuming the spherical magnetization density around the atomic center. This manner of the data analysis may be useful to show the existence of an appreciable amount of the orbital moment for the $3d$ transition ions in some compounds^{4,5} or to know the nature of the actinide magnetism through the deviation of the spin to orbital ratio from the value predicted by Hund's rule.^{6,7} But, the form factor in itself should contain richer information about the asphericity in density distribution. Actually, plenty of knowledge concerning the wave function and the solid-state effects

has been extracted from the neutron magnetic form factor. Why has the x-ray study along this line ever been scarcely done? Looking into this point more in detail, one can see that there exists a rather complicated situation in the x-ray case.

The density distribution of the magnetic scatterers around a specific atom is, in general, affected by the surrounding atomic configuration and, through the spin-orbit coupling, the direction of the magnetic moment as well, which is determined by the interaction within the material and/or an external field. Therefore the anisotropic part of the magnetic form factor depends on the relative orientation between the scattering vector and the crystallographic axes and, moreover, the form factors even of the same reflection indices are no longer identical for different directions of the magnetic moment. These statements are equally applicable to both neutron and x-ray cases. But, in the latter, the spin and orbital contributions to the scattering cross section may also vary in different ways from each other with the above-mentioned geometrical conditions in addition to the x-ray polarization states. Accordingly, the argument on the density asphericity through the x-ray magnetic diffraction is not as straightforward as in the neutron case; in other words, it is difficult to specify which part in the geometry dependence of the form factor comes from changes in the ratio between the spin and orbital contributions and which part is truly attributed to the density asphericity. One of the easy routes, which makes use of the spin-orbital separation property of the x-ray magnetic diffraction, is the aforementioned analysis with the spherical model at the cost of the realistic spatial distribution.

Under the circumstances, the experimental condition where the direction of the magnetic moment is set to be

parallel to the scattering vector is worthy of note. First, the observed magnetic signal comes purely from the spin part of the magnetic moment and does not include the orbital-moment contribution, which is less straightforward to interpret. Second, the spin form factor obtained as a result is directly connected to the atomic density distortion along the moment direction, and easily leads us to the insight into the physical picture. Mathematically speaking, this means that, when the scattering vector \mathbf{k} is taken as the polar axis, $\exp(i\mathbf{k}\cdot\mathbf{r})$ in the atomic scattering factor operator can be expanded into the products of the spherical Bessel function $j_n(kr)$ and the Legendre polynomial $P_n(\cos\theta)$ with the polar angle θ of an electron's position vector \mathbf{r} with respect to the atomic center. The estimate for the P_n term represents the density distortion along the polar axis, which is the moment direction here. Third, as the spin-only form factor often changes its sign at a moderate value of the momentum transfer and the zero-crossing position can be a good indicator for the extent of the form factor, the density modification can be partly examined through the polarity of the magnetic effect even in the case that the quantitative data extraction were not available. The experimental conditions of the Bragg angle, the energy spectrum of the incident synchrotron radiations, etc., are often convenient for the measurement around the zero-crossing position expected for many magnetic ions. Fourth, the undesirable multiple-scattering effect for the ferromagnetic sample can be controlled by the sample rotation about the scattering vector, which does not affect the single-scattering cross section with this special geometry. Fifth, this useful geometry cannot be utilized by the polarized neutron technique, as the scattering cross section vanishes. In view of the first two features, information derived therefrom may be recognized as complementary to that from the so-called magnetic Compton profile.⁸ But, dissimilarly to that, the diffraction phenomenon is site sensitive, and also the antiferromagnetic sample as well as the ferromagnetic one can be investigated with this technique through the $\sigma-\pi$ channel in diffraction.⁹

Up to now, the measurement of such spin form factors has been tried just one time for the ferromagnetic cubic Laves phase compound SmAl_2 (Ref. 10) with the white beam method.^{11,12} The result showed that the spin form factor of Sm^{3+} in this compound is more contracted than the isotropic one, reflecting the prolate distribution of the scatterers, and was consistently interpreted by the mean-field analysis. The thermal variation of the zero-crossing position, however, appears to be counter to the conventional way of thermal averaging and to support the factorized treatment of the relevant operator into the spatial and spin parts (see Sec. II). A similar assumption is usually made in the interpretation of the magnetic Compton profile as well, though the physical meaning of the factorization is unclear. In the light of the usefulness of the spin form factor with this specific geometry as a unique microscopic approach to the electronic state in magnetic materials and the partly enigmatic current status described above, it seems meaningful to theoretically investigate the asphericity effect on this spin form factor for the rare-earth series having well-defined spin and orbital magnetic contributions with both unfactorized and factorized

treatments and, at the same time, to give some guides to the future experimental work at this stage. It is these subjects that we shall deal with in this paper.

In the next section, we first describe the equivalent operator for the present spin form factor, which is the starting point for the subsequent discussion. In Sec. III, the effect of the aspherical density distortion along the moment direction, or the quantization axis for the $4f$ electrons of a rare-earth ion, is estimated as a function of the $4f$ -electron number with respect to the $M=J$ state of the ground J multiplet, where J and M are the quantum numbers for the total angular momentum \mathbf{J} and its z component, respectively. The special cases of Sm^{3+} and Eu^{3+} are dealt with separately in Sec. IV, for which the nearby first excited J multiplet is also taken into account. Section V is devoted to remarks about the thermal variation, especially in the vicinity of the ordering point, and summary is given in Sec. VI. Though, in the concrete estimates presented in Secs. III–V, only the lowest-order asphericity and no crystal fields are considered, we can adequately learn the general trends and how the present spin form factor could be deviated from the isotropic one arising from the spherical component of the density distribution. The full analysis for a specific material will be, if necessary, straightforward.¹⁰

II. EQUIVALENT OPERATOR

The operator corresponding to the present spin form factor is described by $\sum_{\nu} \exp(i\mathbf{k}\cdot\mathbf{r}_{\nu}) s_{z\nu}$, where \mathbf{k} is the x-ray scattering vector, \mathbf{r}_{ν} is the position of the ν th electron, $s_{z\nu}$ is the z component of the ν th electron's spin, and the summation is over the $4f$ electrons. The scattering vector is chosen parallel to the z axis. Expanding the exponential in spherical functions, the following operator equivalence¹³ holds within the subspace indexed by the total orbital and spin angular momentum quantum numbers, L and S , which are determined from the Hund's rule:

$$\sum_{\nu} \exp(i\mathbf{k}\cdot\mathbf{r}_{\nu}) s_{z\nu} = \{\langle j_0 \rangle + \alpha \langle j_2 \rangle O_2^0 + \beta \langle j_4 \rangle O_4^0 + \gamma \langle j_6 \rangle O_6^0\} S_z, \quad (1)$$

where $\langle j_n \rangle$ is the expectation value of the n th-order spherical Bessel function $j_n(kr)$ with respect to the $4f$ radial wave function, O_n^0 is the equivalent operator for the n th-order Legendre polynomial written in terms of the total orbital angular momentum \mathbf{L} , e.g., $O_2^0 = 3L_z^2 - \mathbf{L}^2$, and S_z is the z component of the total spin angular momentum \mathbf{S} . α , β , γ are constants depending on the rare earths. Though the right-hand side of Eq. (1) can be re-expressed using the total angular momentum \mathbf{J} , as will be seen in Sec. V, we leave this physically transparent form as it is for the moment. The spin form factor in question $f_S(\mathbf{k}||z)$ is calculated as the thermal average of the right-hand side of Eq. (1) with the normalization such that $f_S(0) = 1$, and then summarized to be the following familiar form:

$$f_S = \langle j_0 \rangle + c_2 \langle j_2 \rangle + c_4 \langle j_4 \rangle + c_6 \langle j_6 \rangle, \quad (2)$$

where $\langle j_0 \rangle$ denotes the isotropic or spherically averaged form factor and the remaining terms reflect the deviation from the spherical symmetry. Of these asphericity terms, the second-order one is expected to have a major effect in the moderate momentum-transfer region, and, in what follows, we take account only of the $\langle j_0 \rangle$ and $\langle j_2 \rangle$ terms.

Comparing Eq. (2) with Eq. (1), we get

$$c_2 = \alpha \langle O_2^0 S_z \rangle / \langle S_z \rangle. \quad (3)$$

The angle brackets $\langle \dots \rangle$ here denote the expectation value, which may not be confused with the radial integral of $\langle j_n \rangle$. If the spin form factor operator (1) could be properly factorized into the spatial and spin parts, namely $\langle O_n^0 S_z \rangle \rightarrow \langle O_n^0 \rangle \langle S_z \rangle$, c_2 becomes

$$c_2^{(FC)} = \alpha \langle O_2^0 \rangle, \quad (4)$$

just proportional to the quadrupolar charge distortion along the z axis. Our estimates of c_2 in and after the next section are made in these two ways, because it is uncertain at present which treatment is correct, as mentioned in Sec. I. It will be seen, however, in Secs. IV and V that the future experiments on the temperature effect or the materials containing Eu^{3+} may possibly answer this question. Finally, we note the explicit form of α in the present discussion,

$$\alpha = \frac{(2S-7)(4S-7)}{18L(2L-1)}. \quad (5)$$

III. $M=J$ STATE

In this section, we estimate the c_2 coefficient for the $M=J$ state of the ground J multiplet and show how the density asphericity influences the overall shape of the spin form factor and its zero-crossing position. The situation supposed here corresponds to the ordered state at zero temperature, being subjected to no crystal fields, and the one-ion Hamiltonian

$$\mathcal{H} = \lambda \mathbf{L} \cdot \mathbf{S} + \mu_B H (L_z + 2S_z) + 2\mu_B H_{ex} S_z \quad (6)$$

is assumed to be a good description of the system, where λ is the spin-orbit coupling coefficient, μ_B is the Bohr magneton, and H and H_{ex} is the applied and exchange fields, respectively.

Within a manifold of states of constant J , the Wigner-Eckart theorem allows the substitution $\mathbf{S} = (g_J - 1)\mathbf{J}$, and then the expectation value of S_z for the $M=J$ state is

$$\langle S_z \rangle = (g_J - 1)J, \quad (7)$$

where g_J is the Landé factor. Using the explicit forms of the off- J matrix elements of L_z and S_z , and the relation $\langle J | L_z | J \pm 1 \rangle = -\langle J | S_z | J \pm 1 \rangle$,¹⁴ the expectation value of $O_2^0 S_z$ for the $M=J$ state of the ground J multiplet is derived to be

$$\langle O_2^0 S_z \rangle = \frac{(L+1)(J-L)(2L+3)J(2J^2+J+3)}{(J+1)(J+2)(2J+3)} \quad (8a)$$

for the light rare earths, and

$$\langle O_2^0 S_z \rangle = L(J-L)(2L-1) \quad (8b)$$

for the heavy ones. Then, from Eqs. (3), (5), (7), (8a), and (8b), when $\langle S_z \rangle \neq 0$,

$$c_2 = \frac{(2S-7)(4S-7)(L+1)(2L+3)(2J^2+J+3)}{18L(2L-1)(J+2)(2J+3)} \quad (9a)$$

and

$$c_2 = \frac{(2S-7)(4S-7)}{18} \quad (9b)$$

are obtained for the light and heavy rare earths, respectively. Similarly, in the factorized case [Eq. (4)], using

$$\langle O_2^0 \rangle = \frac{(L+1)(2L+3)J(2J-1)}{(J+1)(2J+3)} \quad (10a)$$

and

$$\langle O_2^0 \rangle = L(2L-1), \quad (10b)$$

respectively, $c_2^{(FC)}$ is calculated to be

$$c_2^{(FC)} = \frac{(2S-7)(4S-7)(L+1)(2L+3)J(2J-1)}{18L(2L-1)(J+1)(2J+3)} \quad (11a)$$

for the light rare earths, and

$$c_2^{(FC)} = \frac{(2S-7)(4S-7)}{18} \quad (11b)$$

for the heavy ones. Note that $c_2 = c_2^{(FC)}$ for the heavy rare earths and $c_2 = 0$ for the half filled ions ($4f^7; S = \frac{7}{2}$), such as Eu^{2+} and Gd^{3+} .

In Fig. 1, c_2 and $c_2^{(FC)}$ thus obtained for the rare earths except Sm^{3+} ($4f^5$) and Eu^{3+} ($4f^6$) (see Sec. IV) are plotted as a function of the $4f$ -electron number. It can be seen that the discrepancies between c_2 and $c_2^{(FC)}$ for the light rare earths are also not very much, and that, as a general tendency, the relative contribution of the $\langle j_2 \rangle$ part is important to the rare earths having small values of S , such as Ce^{3+} ($4f^1; S = \frac{1}{2}$), Pr^{3+} ($4f^2; S = 1$), Tm^{3+} ($4f^{12}; S = 1$), and Yb^{3+} ($4f^{13}; S = \frac{1}{2}$). It should be also noted that, for the heavy rare-earth ions, the polarity of the c_2 coefficient is opposite to that of the expectation value of $-\sum_\nu (3 \cos^2 \theta_\nu - 1)$, to which the corresponding aspherical component of the charge scattering amplitude is proportional. This implies that the asphericities of the spin and charge densities are reversed for the more-than-half cases. Figure 2 shows $\langle j_0 \rangle + c_2 \langle j_2 \rangle$ for Pr^{3+} and Dy^{3+} as examples and illustrates how the expected form factors are extended or contracted in comparison with the isotropic cases. For Pr^{3+} , which has a pancake-type charge density, the result is so broad that the zero-crossing position is difficult to be observed. That for Dy^{3+} having the same type of the charge density, on the other hand, falls off more rapidly than the isotropic case and changes its sign for a smaller value of the momentum transfer. Note that the modification of the form factor presented

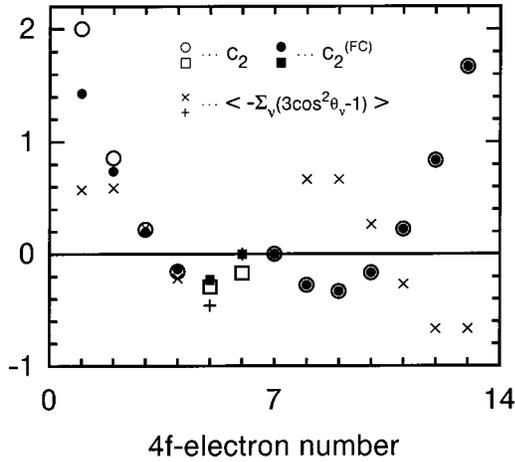


FIG. 1. The c_2 coefficients for the $M=J$ states plotted against the 4f-electron number. Open circles are c_2 of Eqs. (9a) and (9b), and dots are $c_2^{(FC)}$ of Eqs. (11a) and (11b). Crosses denote the expectation values of $-\sum_v(3\cos^2\theta_v-1)$; the positive and negative value means, respectively, the oblate and prolate 4f charge distortion along the quantization axis. For Sm^{3+} ($4f^5$) and Eu^{3+} ($4f^6$), the results estimated in Sec. IV, where the J -mixing effect is taken into account with likely parameters, are shown and marked with different symbols.

here is ascribed to the asphericity of the density distribution and cannot be simply related to the isotropic density spread in real space. A similar anisotropic effect is, more or less, expected for the spin part of the magnetic form factor measured with a general geometry, for the spherical average should be zero. Therefore the analysis, where the spin form factor is approximated to be $\langle j_0 \rangle$, might sometimes lead us to a serious misvaluation of the orbital-moment contribution, especially when the relative size of the orbital moment is very small.

IV. SPECIAL CASES OF Sm^{3+} AND Eu^{3+}

For Sm^{3+} and Eu^{3+} , as the consecutive J multiplets are not well separated energetically, the properties may not be

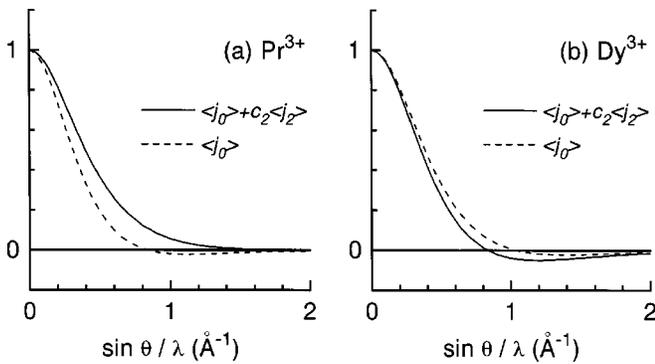


FIG. 2. $\langle j_0 \rangle + c_2 \langle j_2 \rangle$ for the $M=J$ state of (a) Pr^{3+} ($4f^2; L=5, S=1, J=M=4$) and (b) Dy^{3+} ($4f^9; L=5, S=\frac{5}{2}, J=M=\frac{15}{2}$). The values of $\langle j_n \rangle$ are quoted from Ref. 15 and c_2 of Eqs. (9a) and (9b) are used. Broken curves indicate the isotropic parts $\langle j_0 \rangle$ for references.

described, even qualitatively, by the theory considering only the ground J multiplet.¹⁴ In this section, we consider the ground J multiplet admixed with a portion of the excited one via the off- J matrix elements of \mathcal{H} of Eq. (6), and investigate the Sm^{3+} and Eu^{3+} cases.

In a mean-field approximation, the expectation value of S_z for an arbitrary M is self-consistently determined to be¹⁶

$$\langle S_z \rangle = \frac{(g_J - 1)M - 2A_M \mu_B (1 + \delta)H / \Delta_M}{1 - 4A_M \mathcal{J} / \Delta_M}, \quad (12)$$

where J is the one for the ground level, $A_M \equiv \langle J+1, M | S_z | J, M \rangle^2$, \mathcal{J} is the interionic exchange, δ is the enhancement factor for H_{ex} in metals due to the uniform conduction-electron spin polarization caused by H , and Δ_M is the energy interval between the ground and excited levels, which is about 1500 K for Sm^{3+} and 300 K for Eu^{3+} . We neglect here the H and $\langle S_z \rangle$ dependences of Δ_M .

For Sm^{3+} , because $\mu_B H \ll \Delta_M$ for an ordinary external field, the numerator of the right-hand side of Eq. (12) can be approximated by the first term, which means that the admixture of the excited J level through the exchange field results in the modification of $\langle S_z \rangle$ by around a factor of $(1 - 4A_M \mathcal{J} / \Delta_M)^{-1}$. It can be confirmed in the same fashion that such modifications also occur for $\langle O_2^0 S_z \rangle$ and $\langle O_2^0 \rangle$. The effects of the excited level are then estimated to be $\langle S_z \rangle = -1.786 \rightarrow -1.928$, $c_2 = -0.289 \rightarrow -0.291$, and $c_2^{(FC)} = -0.206 \rightarrow -0.229$ for the $M=\frac{5}{2}$ state of Sm^{3+} in a ferromagnet with a Curie temperature of 100 K, i.e., $\mathcal{J} \sim 30$ K, for instance, where the former values are calculated by Eqs. (7), (9a), and (11a), respectively. It seems that $c_2 \propto \langle O_2^0 S_z \rangle / \langle S_z \rangle$ is little modified as the variations of $\langle O_2^0 S_z \rangle$ and $\langle S_z \rangle$ are nearly canceled.

For Eu^{3+} , on the other hand, the second term of the numerator on the right-hand side of Eq. (12) is substantial, for the ground level is $J=M=0$. As for $\langle O_2^0 S_z \rangle$ too, it can be shown that no terms are left but the H -induced one. Thus, for $H \neq 0$, we can get $c_2 = \alpha[3(A_M + A'_M) - L(L+1)] = -\frac{1}{6}$, where $A'_M \equiv \langle J+2, M | S_z | J+1, M \rangle^2$ with J being the ground one. Note that this result depends on neither H nor Δ_M nor \mathcal{J} . Though, from the practical point of view, the size of the induced spin moment is so small, e.g., about $0.04\mu_B$ for $\mathcal{J} = 0$ and $H = 1$ T, that the experiment might be no easy matter or require quite high statistical accuracy, the spin form factor of Eu^{3+} is interesting to measure in terms of the validity of the operator factorization mentioned before. Because, for $\langle O_2^0 \rangle$, all the terms including the H -induced one become zero when $J=M=0$, hence $c_2^{(FC)} = 0$. Then, using the numerical results of $\langle j_0 \rangle$ and $\langle j_2 \rangle$ tabulated in Ref. 15, the values of $\sin\theta/\lambda$ at which the form factor crosses a zero line are evaluated to be 0.84 and 0.94 \AA^{-1} in the unfactorized and factorized cases, respectively. This means that the polarity of the magnetic-diffraction signal with $\sin\theta/\lambda \sim 0.9 \text{\AA}^{-1}$ would enable us to judge which treatment seems true.

The c_2 coefficients estimated in this section are included in Fig. 1 as the typical cases for Sm^{3+} ($4f^5$) and Eu^{3+} ($4f^6$).

V. THERMAL VARIATION

While our argument has been thus far confined to zero temperature, here we examine how the aspherical effect, represented by c_2 , varies with the degree of the magnetic ordering and discuss the thermal variation of the present spin form factor, especially with focusing on the vicinity of the ordering point.

For this purpose, it is convenient to express the right-hand side of Eq. (1) as a sum of the spherical harmonics. For the ground J multiplet, the matrix elements of S_z are proportional to those of $J_1^0 \equiv J_z$, as mentioned in Sec. III, and the product of the components of two tensor operators built up from \mathbf{L} and \mathbf{S} , $O_2^0 S_z$, is expanded into a linear combination of J_1^0 and $J_3^0 \equiv 5J_z^3 - 3J(J+1)J_z + J_z$ as follows:

$$O_2^0 S_z \propto \frac{3}{5} J_3^0 + \frac{2}{5} K J_1^0, \quad (13)$$

where $K = (J+2)(2J+3)$ for the light rare earths and $K = (J-1)(2J-1)$ for the heavy ones. It is well known that, in a mean-field approximation, the thermal variation of $\langle S_z \rangle$ or $\langle J_1^0 \rangle$ is described by the Brillouin function and is of the form $(T_C - T)^{1/2}$ just below the ordering point T_C . On the other hand, $\langle J_n^0 \rangle$ varies as the n th power of $\langle J_1^0 \rangle$ near T_C .¹⁷ Then, in that temperature range, $c_2 \propto \langle O_2^0 S_z \rangle / \langle S_z \rangle$ linearly approaches a finite value determined by J . Rewriting c_2 with respect to the $M = J$ state of Eqs. (9a) and (9b) to be $c_{2,T=0}$, the asymptotic values for the light and heavy rare earths can be described to be

$$c_{2,T \sim T_C} = \frac{2}{5} \frac{(J+2)(2J+3)}{(2J^2+J+3)} c_{2,T=0} \quad (14a)$$

and

$$c_{2,T \sim T_C} = \frac{2}{5} c_{2,T=0}, \quad (14b)$$

respectively. The temperature dependence of c_2 must be then like the solid curves in Fig. 3(a), which shows the mean-field calculated results for Pr^{3+} and Dy^{3+} as examples. At a similar estimate, the contribution of the $\langle j_4 \rangle$ and $\langle j_6 \rangle$ components associated with the higher-order asphericities can be shown to be properly neglected near T_C ; diminishing at most linearly and quadratically as the temperature approaches T_C , respectively.

Attention should be paid here again to the comparison with the behavior of $c_2^{(FC)}$ indicated by the broken lines in Fig. 3(a). In the vicinity of the transition point, $c_2^{(FC)} \propto \langle O_2^0 \rangle$ is reduced with rising temperature in proportion to $\langle J_1^0 \rangle^2$ and becomes 0 at T_C . Therefore, though c_2 and $c_2^{(FC)}$ are not very different at low temperatures (see also Fig. 1), the difference between the two becomes remarkable as the temperature increases. This situation is the realistic case for the ion in the cubic crystal fields, having no corresponding charge

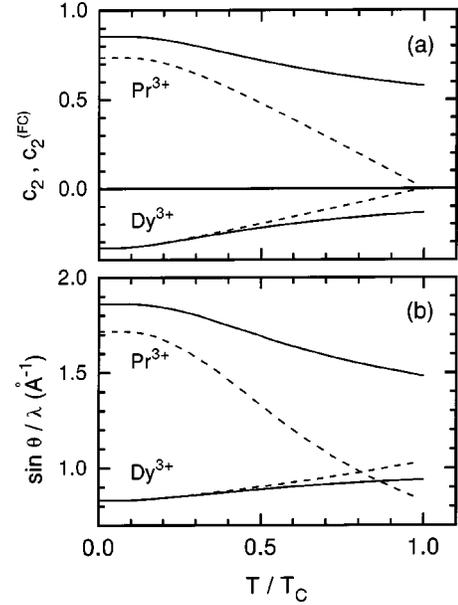


FIG. 3. Calculated thermal variation of (a) c_2 and $c_2^{(FC)}$ [Eqs. (3) and (4)] and (b) the zero-crossing position of $\langle j_0 \rangle + c_2 \langle j_2 \rangle$ and $\langle j_0 \rangle + c_2^{(FC)} \langle j_2 \rangle$ for Pr^{3+} and Dy^{3+} . Solid and broken curves are the results with c_2 and $c_2^{(FC)}$, respectively. \mathcal{H} of Eq. (6) with $H = 0$ and $H_{ex} = -\mathcal{J} \langle S_z \rangle / \mu_B$ is used as the starting Hamiltonian. The interionic exchange \mathcal{J} is set for 30 K, and the resultant Curie temperatures are 16 K for Pr^{3+} and 142 K for Dy^{3+} .

distortion in the paramagnetic regime. The measurement of the thermal shift of the sign-reversal position in the present spin form factor for PrAl_2 , for example, might be then crucial to know the appropriate way of thermal averaging. In Fig. 3(b), the numerical temperature dependence of the sign-reversal position of the form factor in each case is shown.

VI. SUMMARY

The separability of the spin and orbital contributions has been recognized as one of the most striking features of the x-ray magnetic diffraction, as compared to the neutron one, and has attracted many researchers in the relevant field. As described in the introductory section, however, as far as the density distribution study is concerned, further close examination seems to be required from both theoretical and practical points of view. The present study on the spin form factor with the magnetic moment in the target material being parallel to the scattering vector indicates one of the promising courses which we should take in this term. Once the validity of this approach is established from the experimental side, it will become a good complement to the neutron diffraction and the Compton scattering experiments, and may possibly shed light on the novel aspect of the spatial distribution of spin polarization in magnetic materials.

- ¹ M. Blume, J. Appl. Phys. **57**, 3615 (1985).
- ² Doon Gibbs, D. R. Harshman, E. D. Isaacs, D. B. McWhan, D. Mills, and C. Vettier, Phys. Rev. Lett. **61**, 1241 (1988).
- ³ S. P. Collins, D. Laundy, and G. Y. Guo, J. Phys.: Condens. Matter **5**, L637 (1993).
- ⁴ V. Fernandez, C. Vettier, F. de Bergevin, C. Giles, and W. Neubeck, Phys. Rev. B **57**, 7870 (1998).
- ⁵ W. Neubeck, C. Vettier, F. de Bergevin, F. Yakhou, D. Mannix, L. Ranno, and T. Chatterji, J. Phys. Chem. Solids **62**, 2173 (2001).
- ⁶ Masahisa Ito, Fumitake Itoh, Yoshikazu Tanaka, Akihisa Koizumi, Hiroshi Sakurai, Toru Ohata, Koichi Mori, Akira Ochiai, and Hiroshi Kawata, J. Phys. Soc. Jpn. **64**, 2333 (1995).
- ⁷ S. Langridge, G. H. Lander, N. Bernhoeft, A. Stunault, C. Vettier, G. Grübel, C. Sutter, F. de Bergevin, W. J. Nuttall, W. G. Stirling, K. Mattenberger, and O. Vogt, Phys. Rev. B **55**, 6392 (1997).
- ⁸ Nobuhiko Sakai, J. Appl. Crystallogr. **29**, 81 (1996).
- ⁹ M. Blume and Doon Gibbs, Phys. Rev. B **37**, 1779 (1988).
- ¹⁰ H. Adachi, H. Kawata, and M. Ito, Phys. Rev. B **63**, 054406 (2001).
- ¹¹ D. Laundy, S. P. Collins, and A. J. Rollason, J. Phys.: Condens. Matter **3**, 369 (1991).
- ¹² S. P. Collins, D. Laundy, and A. J. Rollason, Philos. Mag. B **65**, 37 (1992).
- ¹³ K. W. H. Stevens, Proc. Phys. Soc., London, Sect. A **65**, 209 (1951).
- ¹⁴ J. H. Van Vleck, *The Theory of Electric and Magnetic Susceptibilities* (Oxford University Press, Oxford, 1932).
- ¹⁵ D. T. Cromer and J. T. Waber, in *International Tables for X-ray Crystallography*, edited by J. A. Ibers and W. C. Hamilton (Kynoch Press, Birmingham, 1974), Vol. IV, Sec. 2.2.
- ¹⁶ A. M. Stewart, Phys. Status Solidi B **52**, K1 (1972).
- ¹⁷ H. Miwa and K. Yosida, Prog. Theor. Phys. **26**, 693 (1961).