Anisotropic spin form factor of $SmAl_2$

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The spin moment associated with the $4f$ unpaired electrons of Sm^{3+} in the cubic Laves phase compound $SmAl_2$ has been selectively measured by the nonresonant coherent elastic scattering (diffraction) of the white synchrotron-radiation x rays. The results have reasonably shown that the spin moment negatively contributes to the sample magnetization and reduces with rising temperature. In addition, it has also been found that the form factor is more contracted than the isotropic case and that the zero-crossing position observed in the form factor varies with temperature. The mean-field analysis with the operator-equivalent technique has adequately described this contraction of the form factor, due to the prolate distribution of the scatterers along the quantization axis, and suggested two possible causes for the thermal shift of the zero-crossing position: the thermal variation of the aspherical $4f$ spin density through the *J*-mixing effect, characteristic to Sm^{3+}, and that of the aspherical $4f$ charge density rather than the spin one concomitant with the magnetic ordering.

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I. INTRODUCTION

When x rays impinge on a magnetic material, the so-called magnetic scattering, due to the relativistic interaction with electrons, occurs in addition to the dominant charge scattering. The magnetic contribution to the diffraction intensity gives the spatial information about the magnetic moment, and the moment arrangement and/or the magnetization density can be determined from it. Another interesting view of the magnetic diffraction is related to the directional nature of a magnetic ion; since the spatial distribution of the magnetic electrons is in general deviated from the spherical symmetry around the atomic center, except for *S*-state ions such as Gd^{3+}, the scattering becomes naturally dependent on the angle between the quantization axis, which can be freezed for a magnetically ordered single crystal, and the x-ray scattering vector.[1,2] This means that the anisotropic properties of the unpaired electrons should be accessible through the magnetic diffraction. Neutron diffraction is a well-established technique used for the similar purpose, whereas x rays are an unique probe to study magnetic materials in that the spin and orbital parts of the magnetic moment can be experimentally separated.[3–8]

From these points of view, the x-ray magnetic diffraction from a ferromagnetic sample with the magnetization being parallel to the scattering vector has some attractive points to be investigated. In the first place, the magnetic effect comes purely from the spin moment and does not include the orbital-moment contribution, which is less straightforward to interpret. Secondly, as will be discussed later, the mathematical formulation of the spin form factor, obtained as a result, becomes greatly simplified and could be connected with the oblate or prolate character of the spin density along the quantization axis. Thirdly, the magnetic diffraction of this geometry cannot be measured in the neutron case, where the scattering cross section vanishes.

The present work on Sm^{3+} in the ferromagnetic cubic Laves phase compound $SmAl_2$ is a serious trial to measure such a spin form factor with white synchrotron-radiation x rays. In the next section, the experimental details are described, and it is shown that the obtained form factor is more contracted than the numerical data for the isotropic case and the zero-crossing position observed in the form factor varies with temperature. These findings are subsequently discussed in Sec. III in comparison with the theoretical calculation using operator equivalences. Conclusions are given in Sec. IV.

II. EXPERIMENTAL

A. Method

The experiment was made at the beamline 3C of the Photon Factory, High Energy Accelerator Research Organization. The adopted method basically follows the technique developed by Collins, Laundy, and Rollason,[9,10] which is characterized by a white beam, a single-crystal sample, and the 90° scattering. Figure 1 shows a schematic layout around the sample. The incident x rays were elliptically polarized light emitted from a bending magnet at a small angle above or below the radiating electron-orbital plane. A single-crystal sample of $SmAl_2$ was set so that the surface normal $\langle 111 \rangle$, which is a direction of easy magnetization, should coincide with the scattering vector, and a series of *hhh* reflections were simultaneously measured by a Ge solid-state detector placed at the sample level in the right-angle direction. The irradiated area on the sample was about 0.2 mm square. The magnetic field of ± 4 kOe applied (anti)parallel to the scattering vector was reversed every 10 sec and the data taking at each temperature lasted 1–5 days. The measurements were done at several temperatures below the sample ordering point of 125 K.

In the present geometry, the fractional change in diffraction intensity upon the reversal of the sample magnetization is given by[10]

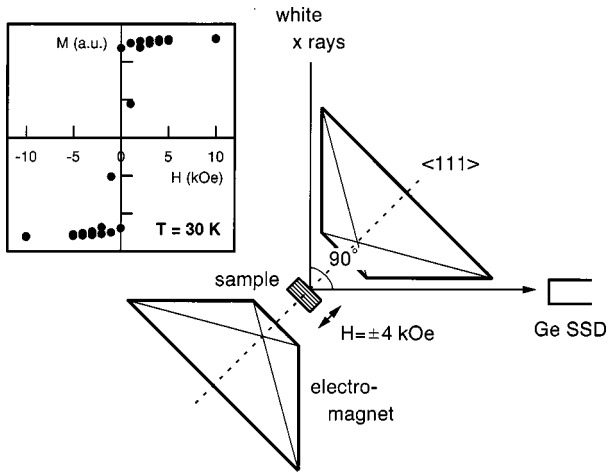

FIG. 1. Schematic layout around the sample (top view). A magnetic field is applied parallel to ⟨111⟩, a direction of easy magnetization, which coincides with the scattering vector. The upper left figure shows the magnetization (M) vs field (H) hysteresis of $SmAl_2$ of the same configuration at 30 K, the lowest temperature in the present diffraction experiment.

$$R=\frac{I_+-I_-}{I_++I_-}=\gamma f_p\frac{\sqrt{2}S(\mathbf{k})}{n(\mathbf{k})}, \tag{1}$$

where γ is the ratio of the incident x-ray energy to the electron rest mass, and $S(\mathbf{k})$ and $n(\mathbf{k})$ are, respectively, the Fourier transforms of the net spin collinear to an external field and charge distributions. The polarization factor f_p is defined as $P_c/(1-P_l)$, and P_c and P_l, here, are the degrees of circular polarization and linear polarization in the scattering plane. To determine f_p, we have separately measured R for Fe (220) reflection as a function of the vertical beam emission angle ψ. By fitting the ψ dependence with the calculation, we have obtained the light source parameters first, and then evaluated f_p at the various values of ψ and photon energies for the practical experiment.[11] Using f_p determined this way and $n(\mathbf{k})$ obtained with the atomic values tabulated,[12] we can derive $S(\mathbf{k})$ and hence the atomic spin form factor $f_S(\mathbf{k})$ multiplied by the net spin moment μ_S.[13] In the present work, owing to the absorption of the low-energy x rays by the Be windows on the beam path, the two inner peaks of 111 and 222 cannot be measured, where the conduction-electron polarization effect might appear.[14] The derived $\mu_S f_S(\mathbf{k})$ can be then ascribed only to the spin polarization of the localized $4f$ electrons of Sm^{3+}.

For the later discussion on the small magnetic asymmetry in the vicinity of the zero-crossing position of the form factor, some technical issues about the derivation of R should be mentioned here. Speaking from our experience, first of all, it is practically crucial to remove the multiple scattering contributions in advance by the sample rotation about the scattering vector. A change of them associated with the field switching or the sample movement results in a substantial bias extrinsic to the magnetic effect and, even if independent of the field direction, such a contribution diminishes R outwardly. In the case that it is impossible in practice to perfectly avoid the traces of the multiple scattering for every diffraction peak simultaneously, we select the best condition for the purpose of the experiment and, at the same time, cannot help giving up obtaining reliable data for some reflections which are relatively unimportant, such as the Al-only ones and a few higher order ones in the present experiment. In the light of the antisymmetric property of the helicity of the incident x rays, or R too, with respect to the orbit plane, it is also quite helpful to measure R equally above and below the orbit plane; the present data were accumulated for these two cases alternately by one or two hours. As long as the sample magnetization is properly reversed by external fields and the magnetic effect is not so extremely small, the general trend of R is usually reversed as expected, and such a sign reversal can be a good indication that the obtained value may be free from artifacts. Needless to say, the size of the receiving slit in front of the detector must be appropriately larger than the diffraction spot, as the intensity measured through the smaller one is affected by a slight sample movement. Finally, to compensate the remaining offset usually not more than around 10^{-3} and to improve the statistical accuracies, the difference profile I_+-I_- is derived by adding the positive-helicity positive-field data and the negative-helicity negative-field one (I_+), and adding the positive-helicity negative-field data and the negative-helicity positive-field one (I_-), and then subtracting one from the other. Fairly weak signals of magnetic origin can be reasonably extracted only after all these procedures.

B. Results

Figure 2(a) shows $\mu_S f_S$ thus obtained. Note the lack of the data points for the *hhh* reflections with $h=4n+2$, which arise only from Al. The minus values for low k peaks mean a negative contribution of the spin moment to the sample magnetization, which is consistent with the previous studies of this compound.[15,16] The decrease of the magnetic effect with rising temperature reflects the reduction of the thermal average of the spin, which is also in accordance with common sense. On the other hand, the shape of the form factor is noteworthy. The form factor at 30 K is obviously more contracted than the isotropic component of the numerical form factor published so far, which is usually denoted by $\langle j_0\rangle$ and crosses a zero line at 0.91–0.93 $Å^{-1}$.[12,17–19] In addition, as the temperature increases, the form factor becomes slightly extended (see the inset). This feature is also clarified by inspection of the temperature dependence of 888 reflection in the vicinity of the zero-crossing position, as is shown in Fig. 2(b).

From the experimental point of view, the most serious problem is thought to be the contamination of the orbital-moment contribution from undesirable magnetic domains. A few percent imperfection of the magnetization reversal shown in the M-H curve (see Fig. 1), however, it is not estimated to be very influential. How about a change of the polarization of the incident x rays or the uncertainty of the estimation? At the present 90° scattering geometry, the normal diffraction intensity itself is a very good monitor for the polarization parameters, and it has been confirmed that such an unexpected change rarely ever occurred during the experi-

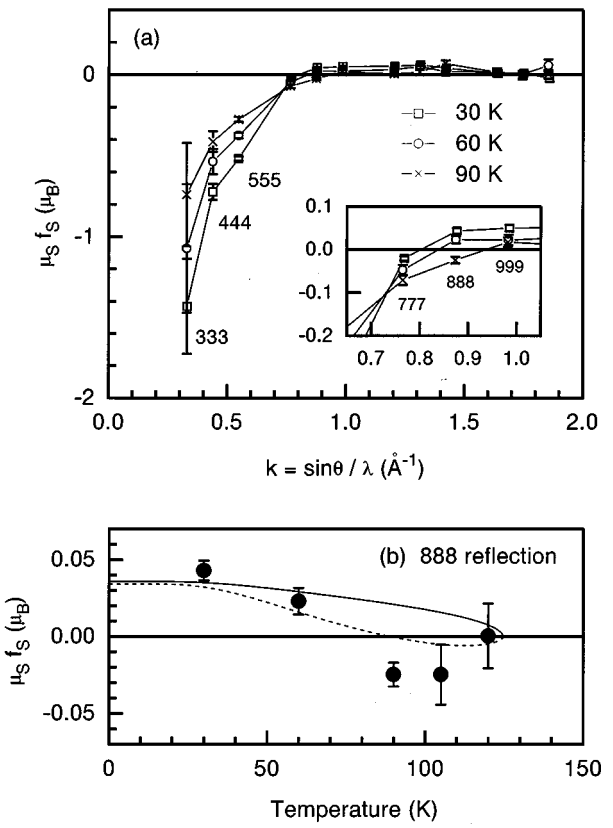

FIG. 2. (a) Observed $\mu_S f_S$ for the $4f$ electrons of Sm^{3+} in $SmAl_2$. The inset is an enlargement around the zero-crossing position. (b) Temperature dependence of 888 reflection. Solid and broken curves show the numerical results (see the text in Sec. III for details). In both figures, error bars denote the statistical accuracy of the experimental data.

ment. In cases where the chart record is questionable, the relevant data are to be excluded from the integration. Moreover, the effect of the change in polarization, to begin with, cannot cause the sign reversal and should be hardly, if ever, influential on the zero-crossing position of the form factor. Thus, this problem also seems not so serious. Other possible artifacts are, as described before, treated with our utmost attention. After all, we cannot find at present any positive reason to doubt the contraction and systematic thermal variation of the form factor observed. In the next section, the behavior in question is theoretically examined in terms of the anisotropic nature of the scatterers.

III. ANALYSIS AND DISCUSSION

Theoretically, when the scattering vector is chosen parallel to the z axis, along which the electron orbitals are quantized, the operator for the spin form factor $\Sigma_i \exp(i\mathbf{k}\cdot\mathbf{r}_i)s_{zi}$ (Refs. 3–6) is expanded as follows:

$$\sum_i \exp(i\mathbf{k}\cdot\mathbf{r}_i)s_{zi} = \sum_n i^n(2n+1) \times\left[\sum_i j_n(kr_i)P_n(\cos\theta_i)s_{zi}\right] \quad (2)$$

with usual notations. Within ^6H ($L=5, S=5/2$), the equivalent operator[20] expressed by the total orbital and spin angular-momentum operators **L** and **S** is derived to be

$$\left[\langle j_0\rangle - \frac{\langle j_2\rangle}{135}O_2^0 + \frac{\langle j_4\rangle}{11550}O_4^0 + \frac{\langle j_6\rangle}{249480}O_6^0\right]S_z, \quad (3)$$

where $\langle j_n\rangle$ is the radial integral of the nth order spherical Bessel function $j_n(kr)$, O_n^0 is the equivalent operator for the Legendre polynomial P_n written in terms of **L**, e.g., $O_2^0 = 3L_z^2 - \mathbf{L}^2$, and the constant coefficients are dependent on the rare earths. Once the eigenvalues and eigenfunctions are determined from the appropriate Hamiltonian, $f_S(\mathbf{k}\|z)$ can be calculated as the thermal average of Eq. (3) with the normalization by the thermal average of S_z, and then expressed in the following form, which is familiar in the neutron-diffraction case:

$$f_S(\mathbf{k}\|z) = \langle j_0\rangle + \sum_{n=2,4,6} c_n\langle j_n\rangle. \quad (4)$$

The first term on the right hand side is the isotropic form factor and the other ones represent the deviation due to the anisotropy. Note that the sign-reversal property relevant to the present problem is inherent in $\langle j_0\rangle$ (see, for example, Ref. 12) and the zero-crossing position of f_S, called k_0 hereafter, is supposed to reflect the relative importance of the $\langle j_2\rangle$ part, which is a dominant component in the region of $\langle j_0\rangle \sim 0$.

Solid lines in Fig. 3 are the numerical results of the temperature dependences for k_0 and the c_n coefficients in Eq. (4). The calculations were done in the same fashion as reported before,[16] using a mean-field approximation and taking into account the lowest two multiplets of $J=\frac{5}{2}$ and $\frac{7}{2}$. As for the parameters required, such as the crystal fields, ones obtained from the magnetic analysis[16] were used. The values of $\langle j_n\rangle$ were quoted from the International Tables.[12] As is shown in Fig. 3(a), k_0 at 30 K agrees well with the experimental value of ~ 0.8 Å^{-1}. Namely, the contraction of the form factor is described by the calculation as originating from the negative value of c_2 or the prolate spin density along the quantization axis. The qualitative trend of the thermal drift can also be reproduced by choosing parameters. Considering that the calculation without the excited multiplet gives k_0 being less variable against temperature, the J-mixing effect seems substantial to the calculated temperature dependence. Compared with experiment, however, the amount of the thermal shift is unsatisfactorily small and the behavior of 888 reflection cannot be reproduced (see Fig. 2). This state of affairs is little improved by any reasonable combination of parameters in the calculation.

The numerical results indicated by broken lines, on the other hand, give much better agreement with experiment, which are obtained by decoupling the spatial and spin parts in Eq. (3). That is to say, these curves are obtained assuming that the form factor is determined from the part in square brackets of Eq. (3) and that S_z contributes only to the scale factor, i.e., $\mu_S = -2\langle S_z\rangle_T$, where the notation $\langle\cdots\rangle_T$ means thermal average. In that case, c_n is just proportional to $\langle O_n^0\rangle_T$

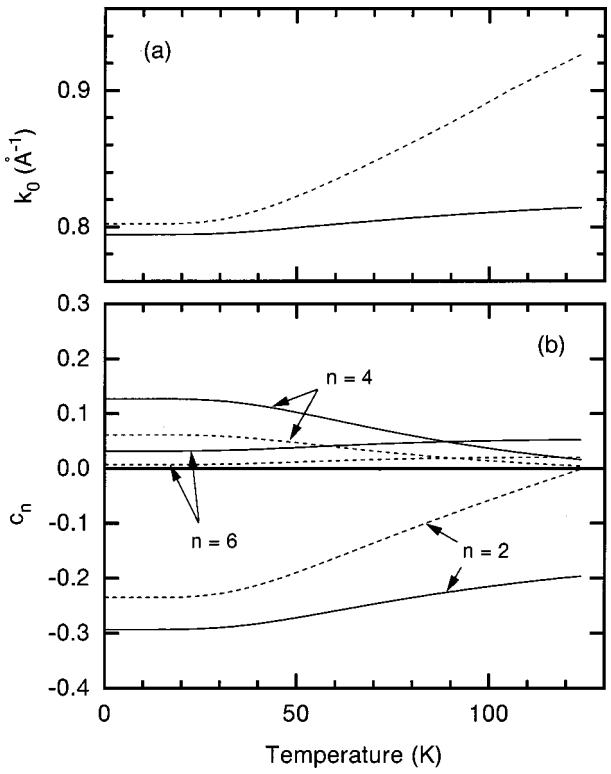

FIG. 3. Numerical temperature dependences of (a) the zero-crossing position k_0 of the spin form factor and (b) the c_n coefficients ($n=2,4,6$) in Eq. (4), which represents the relative importance of the anisotropic term in the form factor. In the calculation, whose results are shown by solid lines, the shape of the form factor is determined from the thermal average of Eq. (3) and c_n is proportional to $\langle O_n^0 S_z\rangle_T/\langle S_z\rangle_T$. Broken lines are, on the other hand, calculated on condition that operator (3) is decoupled into the spatial part put in square brackets and S_z, where c_n is just proportional to $\langle O_n^0\rangle_T$. Parameter set A1 of Ref. 16 is used in the calculation.

instead of $\langle O_n^0 S_z\rangle_T/\langle S_z\rangle_T$, implying that k_0 might be a good indicator for the $4f$ charge distortion, especially for the quadrupole. According to this idea, the phenomenon in question can be interpreted as follows. At low temperatures, k_0 is held down to around 0.8 Å^{-1} due to the prolate distribution of the $4f$ electrons along the quantization axis and, as the temperature approaches the ordering point and $\langle O_2^0\rangle_T$ having a nonzero value in the ferromagnetic region diminishes, it shifts toward the crossover point of the isotropic form factor $\langle j_0\rangle$, i.e., 0.91–0.93 Å^{-1}.[12,17–19] In this manner of calculating, similar results can also be obtained without the excited multiplets. Therefore, such a thermal variation of k_0 might be a common property of the unpaired electrons in the ordered state, not limited to the special case of Sm^{3+}.

The comparison with the experiment appears to support this latter interpretation. But, the physical meaning of the isolation of S_z from operator (3) is incomprehensible at present. It may possibly be suggested that the electron spin in the starting Hamiltonian for the photon-electron interaction could be replaced by its thermal average. However, the relevant scattering seems to take place so quickly that the averaging procedure should be done at the final stage of the calculation together with the spatial part, as has been done in the first analysis, where we did not have a quantitative success. Similar separation of the spin from the momentum distribution is the usual way of analysis the spin-dependent Compton profile, though the validity has not been theoretically established yet.[21,22] With the diffraction approach, the examination of k_0 for the other rare-earth Al_2 compounds might give a good lead to the solution. The observed crossing point may have a mild temperature dependence due to the lack of the J mixing, and again it may show a considerable thermal variation even in the opposite sense to the present case depending on the asphericity of the $4f$ charge cloud. If the latter result is obtained and the thermal variation of k_0 is ensured to reflect $\langle O_2^0\rangle_T$, the present technique might also be useful, for example, to study the system where the quadrupolar interaction works under the magnetic ordering; how the two interaction assist or frustrate each other. The meaning of the operator factorization has to be elucidated separately, though.

IV. CONCLUSIONS

We have measured the $4f$ spin form factor of Sm^{3+} in the ferromagnetic cubic Laves phase compound $SmAl_2$, not including the orbital-moment contribution, by means of white synchrotron-radiation x-ray diffraction, and the following results have been obtained. (1) The spin moment negatively contributes to the sample magnetization, consistent with the previous studies of this compound. (2) The thermal average of the ordered spin reasonably reduces with rising temperature. (3) The form factor at 30 K, the lowest temperature where the experiment took place, is obviously more contracted than the numerical form factor for the isotropic or the spherically averaged case, usually denoted by $\langle j_0\rangle$. (4) The zero-crossing position observed in the form factor varies with temperature $\sim$0.8 Å^{-1} at 30 K and increasing to $>$0.9 Å^{-1} as the temperature increases.

To interpret the findings (3) and (4) regarding the shape of the form factor, we have derived the equivalent operator for the present spin form factor with the angular momentum operators and analyzed the behavior in a mean-field approximation. The calculation has reproduced the experimental contraction of the form factor well and revealed it to be due to the prolate density distribution of the scatterers along the quantization axis. As to the thermal variation of the zero-crossing position or the form factor, two possible causes have been suggested, namely, the thermal variation of the aspherical $4f$ spin density through the J-mixing effect, characteristic to Sm^{3+}, and that of the charge distortion concomitant with the magnetic ordering. To clarify the cause of the present thermal variation, more systematic studies are required.

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