Intra-atomic spin asphericity of Pr and Dy in the dialuminides probed by x rays

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While the theoretical framework of physics today is inevitably accompanied by the concept of electron spin, there has been no useful means to directly see the spatial distribution in solids or atoms so far. We have applied the so-called magnetic x-ray diffraction and succeeded in detecting the aspherical nature of the spin polarization for the atomic electrons of Pr and Dy in the dialuminides. An agreement with the theoretical estimate using the operator technique is fairly good. The present approach may provide unique and valuable data for basic physics and future spin technologies.

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Spin is one of the fundamental attributes of the electron as well as its electric charge, resulting from the combination of relativistic theory and quantum mechanics,[1] and sometimes likened to the self-rotation of the electron for convenience. In many materials, the electrons' spins are not manifest, because there are the same number of electrons rotating in the right- and left-handed ways. In the magnetically ordered systems, on the other hand, the slight unbalance between the two, namely spin polarization, spontaneously occurs. Nowadays the technological application of the spin, such as spintronics, is also being extensively tried. Despite thus widespread recognition of the spin, however, it has been so far no easy matter to observe the real-space distribution of its polarization. High technology today confines itself to managing to distinguish surface spin contrast with atomic resolution.[2] Some people might suspect that such attainments have been already achieved with the famous neutron-diffraction technique long before. But, it should be recalled that the neutron is a tiny magnet and probes the local magnetic field in materials through electromagnetic interaction; that is to say, it is the microscopic magnetization that the neutron sees, which is generated not only by spin polarization but also by the electric current concomitant with the orbital motion of the electrons.

In this note, we report that information about the intra-atomic spin distribution has been successfully obtained with the x-ray diffraction technique instead of the neutron one. Information about the spin distribution is thought to be a favorable comparison to that about the magnetization one in some situations. For example, it is not magnetization but spin that is essential to the emergence of the magnetic ordering in materials,[3,4] and most of the recent *ab initio* calculations for condensed-matter physics lack the convincing implementation to properly take into account or reproduce the effect of the charge-current component of magnetization. If we can know the spatial distribution purely of the spin polarization by some experiment, we will be able to more directly discuss the microscopic state of electrons in magnetic materials without bringing up the "magnetization" in the mutual inspection between experiment and theory, which has a less positive function in the quantum-mechanical world and often makes the analyses complicated.

In principle, at least two kinds of x-ray diffraction experiments seem available to probe the spin polarization, both of which are the branches of the so-called "magnetic" x-ray diffraction. One uses very high energy x rays of an order of 100 keV so that the contribution from the charge-current magnetization should be negligible[5] and the other adopts the special scattering geometry to solely extract the spin

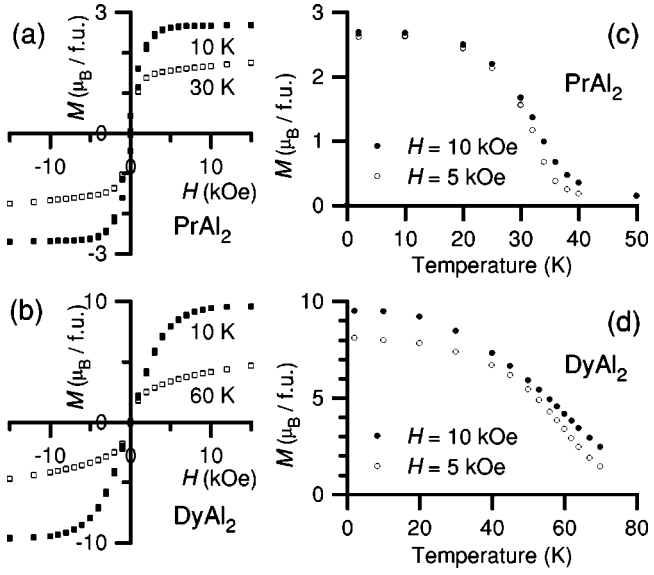

FIG. 1. Magnetization in the ⟨100⟩ direction of $PrAl_2$ and $DyAl_2$ single crystals for magnetic fields applied parallel to ⟨100⟩. The left figures (a, b) show the magnetization (M) vs magnetic field (H) hysteresis, and the right figures (c, d) show the magnetization (M) vs temperature plots. No correction for demagnetizing field is made; in other words, these plots show the actual magnetic response when the external field is applied in the same direction of the same crystal as in the x-ray diffraction measurements. Single crystals were prepared by the Bridgeman method. The magnetic measurements were done using a superconducting quantum interference device magnetometer.

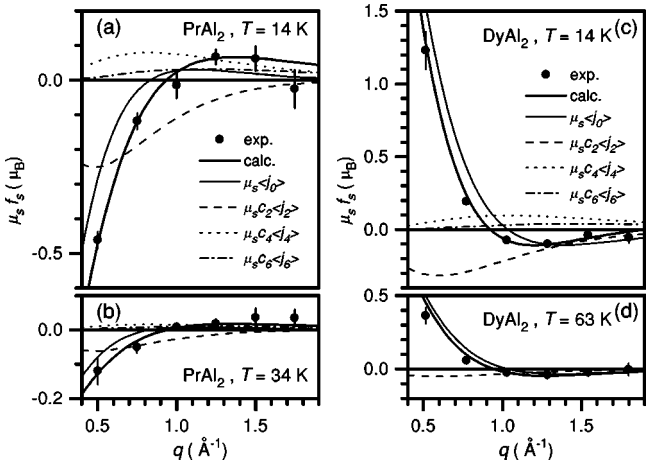

FIG. 2. Atomic spin form factor (f_S) multiplied by spin magnetic moment (μ_S) for Pr in $PrAl_2$ and Dy in $DyAl_2$. In the x-ray diffraction experiments, the samples were set so that the easy direction of magnetization, $\langle 100 \rangle$, should coincide with the scattering vector; a magnetic field of 8.4 kOe was alternately applied parallel and antiparallel to the scattering vector for 20 s each; and a series of $h00$ reflections were simultaneously measured using a white beam and an energy-dispersive detector (Ge SSD). Data-accumulation time is a few days for the measurement at each temperature. The atomic spin form factors are obtained from the fractional change in diffraction intensity upon the reversal of the sample magnetization. Displayed are the data for $h=8$, 12, 16, 20, 24, and 28, which are the crystallographically allowed reflections. In theory, on the other hand, the following mathematical expansion can be made for the form factor of the $4f$ electrons, $f_S=\langle j_0 \rangle + c_2\langle j_2 \rangle + c_4\langle j_4 \rangle + c_6\langle j_6 \rangle$, where $\langle j_n \rangle$ is the expectation value of the nth-order spherical Bessel function with respect to the $4f$ radial wave function. Of these terms, $\langle j_0 \rangle$ means the spherical component and the others represent the aspherical effect of the nth order. Calculated results are shown together with these components. Note that the displayed curves are not the fitting results to the experiment but the results calculated with the appropriate values of the crystal-field parameters and the interionic exchange interaction. For the crystal fields, the values in Ref. 9 are used, and the interionic exchange is determined so as to reproduce the observed magnetic ordering point.

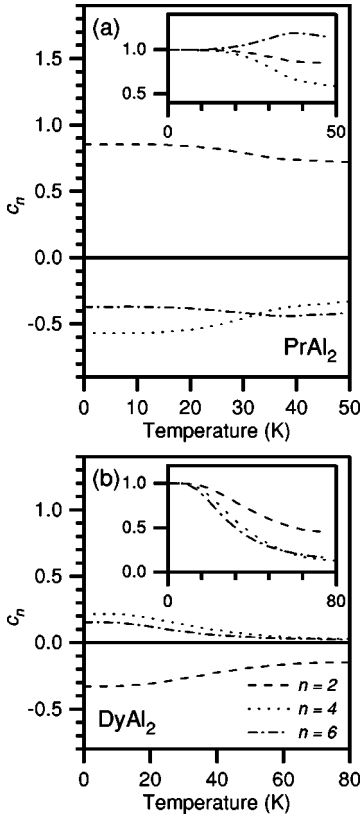

FIG. 3. Calculated temperature dependences of the aspherical effects on the atomic spin form factors of Pr in $PrAl_2$ and Dy in $DyAl_2$, represented by c_n. A definition of c_n is given in the caption of Fig. 2. The insets show the temperature dependencies normalized by the values at 0 K. Thermal variations of c_n imply that the general feature of the form factors, or the spatial distribution of the spin polarization, varies with temperature. For example, according to the calculation for $PrAl_2$, the relative contribution of the fourth- and sixth-order asphericities becomes smaller and larger as the temperature increases, respectively. This means that a broad maximum in form factor as observed around $q \sim 1.3$ Å^{-1} at 14 K would shift toward higher-q region at higher temperatures, and such behavior is actually found in the experimental observation [Figs. 2(a) and 2(b)].

contribution.[6] We have used this latter technique and studied the atomic spin distribution within the rare-earth ions having considerable charge-current magnetization.

The samples we used are the ferromagnetic intermetallics $PrAl_2$ and $DyAl_2$ having the same cubic crystallographic structure. The method is white-beam diffraction[7,8] with the sample magnetization being parallel to the scattering vector, which is almost the same as has been adopted in our previous trial.[6] In the present work, however, some improvements have been made concerning the magnitude of the applied magnetic field, the corrections made in the data analysis, and so forth. The details will appear in a separate paper. Experiments were done at the station 3C3 of the synchrotron-radiation facility, Photon Factory, in Tsukuba, Japan. According to Hund's rule, the $4f$ electrons of Pr and Dy, mainly responsible for their magnetic properties, have similar pancake-type (oblate) charge densities, and the easy direction of magnetization for both dialuminides is the $\langle 100 \rangle$ direction of the crystallographic structure.[9] What is of interest is therefore how their spin densities are and how different from or similar to each other they are.

Figure 1 shows the results of the macroscopic magnetic measurements. The magnetization versus magnetic field hysteresis plots [Figs. 1(a) and 1(b)] show that the field strength of ~8.4 kOe, which was used in the x-ray diffraction measurements, is enough to reverse the magnetization for both samples. Figure 2 shows the obtained atomic spin form factors at 14 K and around the magnetic ordering points as a function of $q=\sin\theta/\lambda$, where θ is the Bragg angle of diffraction and λ is the wavelength of x rays. Atomic form factors are the original data for the intra-atomic structure analysis with the diffraction technique, and information on the real-space distribution of the scatterers can be extracted therefrom. Smooth lines are the numerical results with the $4f$ radial wave functions calculated by the relativistic Hartree-Fock method,[10] the aspherical effects evaluated with the operator-equivalent technique,[6,11] and the interionic interaction in a mean-field approximation. Bold lines are the spin

form factors of the $4f$ electrons and the others represent the spherical component and the aspherical ones of the second, fourth, and sixth orders in mathematical expansion.

We can learn various properties of the spin distribution in question from these results. In a low-q region, the spin form factors of Pr and Dy have negative and positive values, respectively. This unveils their negative and positive polarities of the spin contribution to the total magnetization including the charge-current component, being consistent with Hund's rule. In comparison with the spherical form factors, the experimental ones are somewhat extended and contracted for Pr and Dy, changing their signs at higher and lower values of q, respectively. It can be seen that the aspherical effects of the second order are responsible for such shifts of the zero-crossing positions. The second-order asphericity here represents the ellipsoid-of-revolution-type density distortion and, roughly speaking, the present results indicate that, while the spin polarization of Pr has an oblate distribution similar to the charge density, that of Dy has a prolate one. This difference arises from the fact that, as the $4f$ orbitals of Dy are more-than-half filled, the spin asphericity for Dy is determined by the vacant orbitals, i.e., holes. According to the theoretical analysis, if considering only the aspherical effect up to the second order, the spin form factors or the zero-crossing positions would be more drastically modified from the spherical cases.[11] Actually, however, it seems that higher-order effects partly cancel the second-order one so that the deformation of the form factors is not very much. The experiments, furthermore, tell us the temperature dependence not only in the scale factor, namely the absolute value of the spin magnetization (μ_S in Fig. 2), but also in the general feature of the form factors. This implies that the spin polarization changes its spatial distribution together with the degree of ordering. In our method of data analysis, this phenomenon can be examined as the thermal variation of the relative contributions of the aspherical components (Fig. 3).

An experimental study on the real-space distribution of the spin polarization seems thus to largely extend our microscopic knowledge of the magnetic materials and/or atoms. Though here we treated the typical cases with appreciable charge-current magnetization and gave demonstrative descriptions, the present approach may enable in future closer inspection of more delicate problems, such as the relativistic effect on the spin density, the exchange-correlation effects among the electrons, the distribution of the core-electron polarization, and many other solid-state effects. On the other hand, in recent years, we have been trying to utilize the spin for many technological applications, too. Considering the current trend of nanoscience or spin manipulation, the importance of the work of this sort may be increased. The present approach may not promote the forefront of technology in a direct manner but, as a steady basic research, it could contribute to the establishment of a foothold and the development of new aspects.

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