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Magnetic Compton scattering study of Laves phase $ZrFe_2$ and Sc doped $ZrFe_2$: Experiment and Green function based relativistic calculations

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ABSTRACT

Spin momentum densities of ferromagnetic $ZrFe_2$ and $Zr_{0.8}Sc_{0.2}Fe_2$ have been measured using magnetic Compton scattering with 182.65 keV circularly polarized synchrotron radiations. Site specific spin moments, which are responsible for the formation of total spin moment, have been deduced from Compton line shapes. At room temperature, the computed spin moment of $ZrFe_2$ is found to be slightly higher than that of Sc doped $ZrFe_2$ which is in consensus with the magnetization data. To compare the experimental data, we have also computed magnetic Compton profiles (MCPs), total and partial spin projected density of states (DOS) and the site specific spin moments using spin-polarized relativistic Korringa-Kohn-Rostoker method. It is observed that the spin moment at Fe site is aligned antiparallel to that of Zr site in both $ZrFe_2$ and $Zr_{0.8}Sc_{0.2}Fe_2$. The MCP results when compared with vibrating sample magnetometer based magnetization data, show a very small contribution of orbital moment in the formation of total magnetic moments in both the compounds. The DOS of ferromagnetic ground state of $ZrFe_2$ and $Zr_{0.8}Sc_{0.2}Fe_2$ are interpreted on the basis of a covalent magnetic model beyond the Stoner rigid band model. It appears that on alloying between a magnetic and a non-magnetic partner (with low valence), a polarization develops on the non-magnetic atom which is anti-parallel to that of the magnetic atom.

1. Introduction

The Laves phase (C15) structural intermetallics with formula (AB_2; A and B are 3d/4d transition metals) exhibit very interesting electrical, magnetic and alloying properties [1]. In this series, the $ZrFe_2$ compound shows peculiar physical and magnetic properties. Yamada and Shimizu [2] have studied the density of states (DOS) for *d* electrons in the C15 intermetallic compounds $ZrFe_2$, $LuFe_2$ and $HfFe_2$ in their paramagnetic and ferromagnetic states using a tight-binding approximation. Klein et al. [3] have computed self-consistent paramagnetic electronic structure of ZrV_2, $ZrFe_2$ and $ZrCo_2$ using the augmented-plane-wave (APW) method with local density approximation (LDA). They have also discussed about the spin susceptibilities and magnetic moments of these compounds. The magnetic moments and hyperfine fields of different 3d impurities diluted in $ZrFe_2$ intermetallic compounds have been computed by Oliveira et al. [4]. Using self-consistent spin polarized calculations, Mohn and Schwarz [5] have concluded that ferromagnetic state of $ZrFe_2$ and YFe_2 is more stable than paramagnetic state. Hyperfine fields of Laves phase compounds were calculated by Asano and Ishida [6] using the linearized muffin-tin orbitals (LMTO) method with local spin density approximation (LSDA). The authors have compared their results with neutron diffraction data. Single-crystal neutron diffraction studies of magnetization density in $ZrFe_2$ have been reported by Warren et al. [7] using both polarized and unpolarized incident beams. The authors have also reported the Curie temperature of this material as 604 K and the saturation magnetization of 3.46 μ_B/f.u. at 4.2 K. The binding energy and site preference of hydrogen in ZrX_2 (X = V, Cr, Mn, Fe, Co, Ni) Laves phase compounds have been investigated by Hong and Fu [8] using first-principles LDA and generalized gradient approximation (GGA) approaches. Authors have found a large magnetic moment (0.5 μ_B) at Zr site which is antiparallel to the moment at Fe site (1.9 μ_B) in H-free $ZrFe_2$ compound. Chang-Wen et al. [9], using the APW plus local orbital method approach, obtained the DOS and magnetic properties of $ZrFe_2$. The local magnetic ordering in $ZrFe_2$ doped with deuterium has been studied by

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Wiesinger et al. [10]. Legoas et al. [11] computed the site preference and local moments for 3d impurities in the $ZrFe_2$ and analyzed their results using nuclear magnetic resonance experiments.

In the present manuscript, we employ a versatile technique namely magnetic Compton scattering (MCS) [12,13] to deduce the spin polarized momentum density in $ZrFe_2$ and Sc doped $ZrFe_2$ compounds at room temperature. The MCS is based on inelastic X-ray scattering of circularly polarized radiations with the unpaired electrons under the influence of external magnetic field. The measured spectra (difference of spin-up and spin-down spectra) is known as magnetic Compton profile (MCP), $J_{mag}(p_z)$. Theoretically, $J_{mag}(p_z)$ is the difference of one dimensional projection of unpaired (magnetic) momentum density deduced from majority- and minority-directions of electron spins [12,13],

$$J_{mag}(p_z) = \int\int [n_{maj}(\vec{p}) - n_{min}(\vec{p})]dp_x dp_y. \quad (1)$$

Here, $\vec{p}[= (p_x, p_y, p_z)]$ is the momentum of an electron in a solid and $n_{maj}(\vec{p})[n_{min}(\vec{p})]$ denotes momentum density with majority-[miniority-] spin.

To compare experimental MCPs, we have also computed theoretical MCPs and spin moments using spin polarized relativistic Korringa-Kohn-Rostoker (SPR-KKR) method. Manifold objectives of present study are:

a. To measure the isotropic spin momentum densities of $ZrFe_2$ and $Zr_{0.8}Sc_{0.2}Fe_2$ and to study the role of individual elements in formation of magnetic response of these compounds.
b. To compare MCPs with magnetization data, which enables to explore the role of orbital moment in formation of total magnetic moment.
c. To validate the experimental MCPs by comparing them with the theoretical MCPs (computed using SPR-KKR calculations).
d. To explore nature of magnetism on the basis of total and partial spin polarized DOS.

2. Experiment

Measurements on MCPs were undertaken using circularly polarized synchrotron radiations (SRs) at the beam line BL08W of SPring-8, Japan [14]. The incident SRs having 182.65 keV energy and an on-axis degree of circularly polarization of 0.55 were selected. The back scattered (178°) SRs were energy analyzed using a ten-segment Ge solid-state detector (Canberra, model GL0115S). An overall momentum resolution (full width at half-maximum (FWHM)) of the spectrometer was found to be 0.4 a.u. The spin-dependent Compton signal was deduced by reversing the magnetization of sample in the sequence ABBAABBA... (A and B indicate the spin-up and -down directions, respectively). The externally applied magnetic field of ±2.5 T was reversed after every 60 s. To obtain absolute MCP data, the raw data were corrected for energy dependent corrections like, detector efficiency, absorption and the magnetic cross-section corrections, etc. In such experiments, the effect of multiple scattering is neglected because the spin-dependent multiple scattering contribution is very small [12,15]. Thereafter, the data were converted from energy to momentum scale. Lastly, the respective Compton profiles were normalized to spin moment (per formula unit) of $ZrFe_2$ and $Zr_{0.8}Sc_{0.2}Fe_2$ compounds. The normalization of MCPs of the measured samples was determined using MCP of standard Fe sample, measured under the similar experimental arrangement [16,17]. The spin moments of both the samples were deduced using the relation,

$$\mu_{Sample} = \left[\frac{A_{Sample}}{A_{Fe}}\right] \times \left[\frac{R_{Sample}}{R_{Fe}}\right] \times 2.16\mu_B. \quad (2)$$

In Eq. (2), A is the number of electrons contributing in the inelastic scattering phenomenon, R is the magnetic effect which is ratio of magnetic signal to charge signal of measured data and 2.16 μ_B is standard magnetic moment of Fe calibrator. The electrons participating in Compton phenomenon in the momentum range −10 to +10 a.u. corresponding to $ZrFe_2$ and $Zr_{0.8}Sc_{0.2}Fe_2$ were 84.43 and 81.26 e^-, respectively, while those for Fe the number of electrons was found to be 24.32 e^- [18]. From the measured MCP of Fe, the R_{Fe} was found to be 0.019694. The magnetization data (M–T) were also measured using vibrating sample magnetometer (VSM - 14 T PPMS).

3. SPR-KKR calculations

To analyze experimental spin momentum densities, we have calculated the theoretical MCPs using SPR-KKR code [19]. In KKR method, Green's function using multiple scattering theory is employed. The self-consistency was achieved using exchange-correlation potentials as suggested by Perdew et al. [20] in the framework of GGA [20]. It is worth noting that the GGA plays a crucial role in stabilizing correct magnetic structures of 3d transition metals [21]. The non-overlapping muffin-tins (MT) of radii 2.77 and 2.36 a.u. have been used for Zr and Fe, respectively. The experimental lattice parameters for cubic $ZrFe_2$ and $Zr_{0.8}Sc_{0.2}Fe_2$ were taken to be 7.072 and 7.053 Å, respectively [22]. The angular momentum expansion for the major component of wave function (l_{max}) was restricted to standard value as 2. For a faster convergence, the SCF mixing parameter in BROYDEN2 algorithm was kept as 0.2 and Ewald parameter was taken to be 0.30. In self consistency process, 1330 **k** points were generated within the **k** mesh of (26 × 26 × 26) for $ZrFe_2$ and $Zr_{0.8}Sc_{0.2}Fe_2$. To derive the spherically averaged MCPs, we have computed the directional MCPs for both compounds along six low-indexed directions namely [1 0 0], [1 1 0], [1 1 1], [2 1 0], [2 1 1] and [2 2 1] [23,24]. To calculate the spherically averaged MCPs from the directional MCPs of high symmetric directions, we have used the following two relations [23,24]:

$$J(p_z) = [10 * J_{100}(p_z) + 16 * J_{110}(p_z) + 9 * J_{111}(p_z)]/35 \quad (3)$$

$$J(p_z) = 0.0722 * J_{100}(p_z) + 0.2170 * J_{110}(p_z) + 0.2367 * J_{111}(p_z) + 0.1154 * J_{210}(p_z) + 0.2276 * J_{211}(p_{z,}) + 0.1312 * J_{221}(p_z) \quad (4)$$

The spherically averaged theoretical $J_{mag}(p_z)$ were convoluted with a Gaussian FWHM of 0.40 a.u., to incorporate the effect of instrumental resolution.

4. Results and discussion

The experimental MCPs of undoped and doped $ZrFe_2$ at 300 K under 2.5 T magnetic fields are shown in Fig. 1. The MCPs were normalized to experimental spin magnetic moment deduced from Eq. (2). It is known that the MCP provides the spin magnetic moments at different sites of constituent elements by splitting the $J_{mag}(p_z)$ into individual components. To deduce the individual spin moment contribution at different sites, the isotropic MCPs of $ZrFe_2$ and $Zr_{0.8}Sc_{0.2}Fe_2$ were fitted with the spherically averaged MCP of Fe (computed using SPR-KKR method by taking spherical average of 6 different directions as mentioned in Eq. (4)), free atom Compton profile of Zr-4d electrons, and diffuse (Zr-5 s^2 electrons for $ZrFe_2$; and Zr-5 s^2, Sc-3d^1, Sc-4 s^2 electrons for Sc doped $ZrFe_2$) profile. The diffuse profiles were modeled using a Gaussian shape with a FWHM of 0.82 a.u. and 0.85 a.u. for $ZrFe_2$ and $Zr_{0.8}Sc_{0.2}Fe_2$, respectively. It is worth noting that the above mentioned FWHM