Verification of Ni magnetic moment in $GdNi_2$ Laves phase by magnetic circular dichroism measurement

M. Mizumaki
JASRI, SPring-8, Kouto, Mikazuki, Sayo, Hyogo 679-5198, Japan

K. Yano
C.S.T., Nihon-University, Funabashi, Chiba 274-8501, Japan

I. Umehara
Faculty of Engineering, Yokohama National University, Yokohama 240-8501, Japan

F. Ishikawa
Institute for Solid State Physics, University of Tokyo, Kashiwanoha, Kashiwa, Chiba 277-8581, Japan

K. Sato
Faculty of Engineering, Fukui Institute of Technology, Fukui, Fukui 910-8507, Japan

A. Koizumi and N. Sakai
Faculty of Science, Himeji Institute of Technology, Akou, Hyougo 678-1297, Japan

T. Muro
JASRI, SPring-8, Kouto, Mikazuki, Sayoh, Hyogo 679-5198, Japan
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Investigation of the magnetic moment of nickel in the polycrystal $GdNi_2$ Laves phase was carried out by means of magnetic circular dichroism (MCD) in the core-level x-ray-absorption spectroscopy. It was revealed that the nickel magnetic moment originating from the $3d$ state (band) does exist and couples antiparallel to that of gadolinium whose MCD was observed at the $M_{4,5}$ absorption edge. That is, nickel retains an intrinsic magnetic moment even in the Laves phase concentration. Furthermore, by analyzing in terms of sum rule, the contribution of spin and orbital magnetic moments to the magnetic moment was evaluated and discussed.

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Regardless of crystalline and noncrystalline, transition-metal–rare-earth (RE) alloys have been an interesting subject in magnetism especially from the 1960s to 1980s. The combination of a transition metal (TM) with an itinerant nature and the RE of well localized $4f$ electrons, including outer-shell electrons, is fascinating to many investigators. Consequently, numerous papers have been published and some important pictures in TM-RE magnetism have been established. One of the well-known establishments is the disappearance of the magnetic moment of nickel in RE Ni_2 as the RE content increases up to Laves phase and this phenomenon can be seen in some notable review papers.[1–3] This result, which was supported by neutron-diffraction observation on $TbNi_2$, has become well established. Based on the result, the following picture has been drawn that the $3d$ band of nickel is gradually filled by the outer-shell electrons of the RE. Subsequently, some band calculations have been carried out and it seems to have supported this result and picture.[3,4]

In 1997, on the other hand, Mallik *et al.* have investigated the inverse susceptibility for $(Gd_{1-x}Y_x)Ni$ intermetallic compounds and detected an excess effective moment. They attributed the excess one to a Ni magnetic moment and suggested that nickel has a magnetic moment induced by Gd where Gd and the induced Ni couple ferromagnetically.[5] Further in 1999, Yano *et al.* noticed the scatters of magnetic data including the Curie temperatures and made the magnetic Compton profile measurements on GdNi single crystal aiming at detecting the magnetic moment of Ni. However, they did not obtain a decisive result.[6] Therefore, we selected the magnetic circular dichroism (MCD) in the core-level x-ray absorption spectoscopy (XAS) to extract only the magnetic moment of Ni in intermetallic compounds because MCD in XAS is an element-selective method. The MCD in XAS, namely, the difference of the spectra between parallel and antiparallel geometries of the sample magnetization and the photon spin of the incident circularly polarized light, has recently been used for the study of ferromagnetic and ferrimagnetic materials.

XAS is not only an element-specific method but it also yields information about a specific orbital through which the core electron is strongly excited due to the selection rule and the transition probability. As a transition metal the $3d$ orbital, which is the main origin of the magnetic moment, can be probed directly by $2p$ XAS. It is also known that MCD signals yield a quantitative value for the orbital magnetic moment as well as the spin magnetic moment using sum rules.[7,8]

In this paper, we report that the Ni in $GdNi_2$ has a clearly finite magnetic moment and that the magnetic moment of Gd and Ni couples antiferromagnetically.

Polycrystalline samples of $GdNi_2$ were prepared from Gd metals of 99.9% purity and Ni metals of 99.999% purity by arc melting under a pure argon atmosphere. The ingots obtained were annealed for three days at 900, and x-ray powder diffraction at room temperature showed only reflections of a cubic C15 Cu_2Mg-type crystal structure. The obtained ingots consisted of fairly large single-crystalline grains, which shows the high quality of these polycrystalline samples.

MCD and XAS spectra at the Ni $L_{2,3}$ edges and the Gd $M_{4,5}$ edges were measured for $GdNi_2$ using synchrotron radiation at soft x-ray beamline BL25SU of SPring-8, Japan. The optical system of BL25SU is a varied space plane grating type monochromator. The energy resolution was set to be $E/\Delta E > 7000$ at around 870 eV.

The XAS spectrum was measured by the total electron yield (TEY) method in which the sample current is directly measured while the photon energy is scanned. It is empirically known that the TEY spectrum is a good representation of a photoabsorption spectrum in the core-level excitation region. The MCD spectrum was taken by reversing the direction of the magnetic field $H=1.4$ T applied to the sample at each photon energy while keeping the helicity fixed. We defined the MCD spectrum as $I_+ - I_-$, where I_+ and I_- denote the absorption intensities with the photon spin parallel and antiparalle to the direction of the magnetic field, respectively. The XAS spectra were obtained on surfaces filled in an ultrahigh vacuum of 5×10^{-8} Pa. The photon energy for the XAS spectra was calibrated with respect to the Fermi edge of an evaporated gold thin film. We carried out measurements of the XAS-MCD spectra for $GdNi_2$ at $T=25$ K, which is much lower than its Curie temperature (T_c).

Figure 1 shows the Ni $2p\rightarrow3d$ XAS spectra, I_+ and I_-, and their MCD spectra, $I_+ - I_-$, for $GdNi_2$. The XAS spectra consist of the L_3 and L_2 components split by the spin-orbit interaction of the core hole. In the L_3 region, the XAS spectra have three peaks, denoted by *A*, *B*, and *C*, and these XAS spectra are qualitatively similar to those of pure Ni metal.[9,10] In the higher-energy region above peak *B*, however, the XAS spectra shown in Fig. 1 have more complicated structures than those of pure Ni metal. In the L_2 region, on the other hand, the XAS spectra have a main peak of *D* and subpeaks of *E* and *F*, as in the L_3 region. However, the width of the three peaks in the L_2 region was broader than that of the peaks in the L_3 region. This result can be ascribed to the lifetime broadening effect stemming from the uncertainty principle because the lifetime of the core hole at the L_2 edge is much shorter than that of the L_3 edge due to the Coster-Kronig decay. The MCD spectrum in the L_3 region shown in Fig. 1 has three clear peaks A', B', and C', which correspond to *A*, *B*, and *C*, in XAS, respectively. This result means that Ni in $GdNi_2$ has an obviously finite magnetic moment. Peak A' is a positive peak, and peak B' is a dispersion type. Following Jo and Sawatzky,[10] we propose the following peaks assignment. Peaks A (A') and D (D') correspond to the $2p^6 3d^9 \rightarrow 2p^5 3d^{10}$ transition. Peaks B (B'), C (C'), and E (E') correspond to the eigenstate of the $2p^5 3d^9$ configurations at the final state. According to Manini

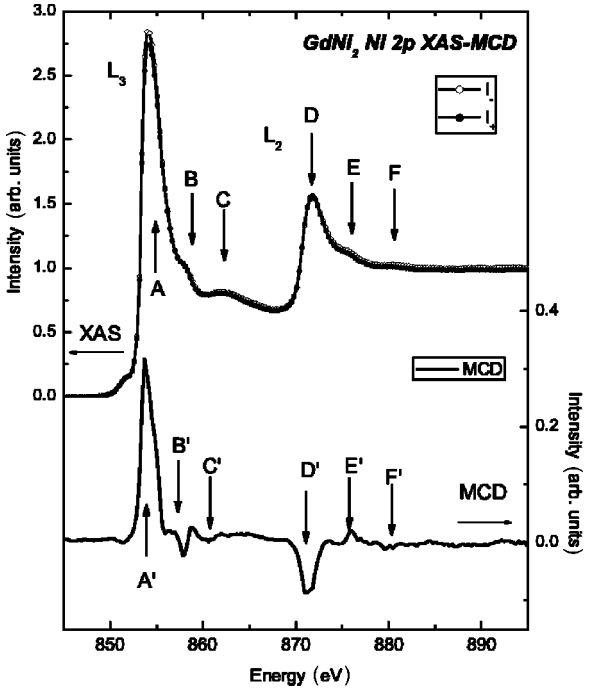

FIG. 1. Ni $2p\rightarrow3d$ XAS-MCD spectra in $GdNi_2$ at $T=25$ K. Solid circles (I_+) and open circles (I_-) show the XAS spectra which have magnetizations antiparallel and parallel to the photon spin. The solid lines in the lower panel show the MCD spectra.

et al.,[11] these satellite peaks (*B*, *C*, and *E*) in Ni XAS-MCD spectra mean that Ni $3d$ holes have an X_2 character. That is to say, we think that Ni $3d$ holes in $GdNi_2$ have an X_2 character. According to Laan *et al.*,[12] peak *C* corresponds to the eigenstate of the $2p^5\ t_{2g}$ configurations at the final state. They show in theoretical calculation that the energy difference between peak *B* and peak *C* increases in proportion to the crystal field. The anisotropic hybridization is practically the same effect of the crystal field. Therefore, we could think that peak *C* corresponds to the eigenstate of the $2p^5\ t_{2g}$ configurations at the final state.

Figure 2 shows the Gd $3d\rightarrow4f$ XAS spectra, I_+ and I_-, and their MCD spectra, $I_+ - I_-$, for $GdNi_2$. The XAS spectra consist of the M_5 and M_4 components split by the spin-orbit interaction of the core hole. In both the M_5 and the M_4 region, the XAS spectra have many structures that are due to the multiplet effect. The magnitude of the MCD effect is very large and 50% of the XAS intensity at 1186 eV. In order to interpret these experimental spectra, we calculated the $3d\rightarrow4f$ XAS and MCD spectra by means of the complete atomic multiplet method. (The calculational details are shown in Refs. 13 and 14.) The theoretical spectra (Fig. 2, inset) reproduce these experimental XAS and MCD spectra very well. This result means that the Gd in $GdNi_2$ is trivalent and that $4f$ state of Gd is close to $^{7/2}S$.

Let us consider the meaning of the MCD's sign. In the Ni $2p\rightarrow3d$ XAS-MCD, the sign is positive in the L_3 region and negative in the L_2 region. In the Gd $3d\rightarrow4f$ XAS-MCD, the sign is negative in the M_5 region and positive in the M_4 region. This means that the magnetic interaction between Gd and Ni is an antiferromagnetic coupling. Therefore, we con-

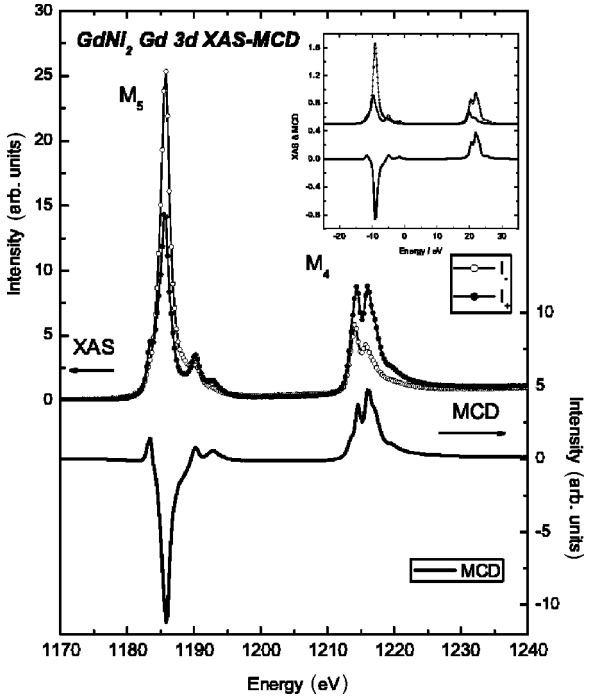

FIG. 2. Gd $3d \rightarrow 4f$ XAS-MCD spectra in $GdNi_2$ at $T=25$ K. Solid circles (I_+) and open circles (I_-) show the XAS spectra which have magnetizations antiparallel and parallel to the photon spin. The solid lines in the lower panel show the MCD spectra. The inset shows the theoretical XAS spectra (upper) and MCD spectra (lower).

cluded that $GdNi_2$ is a ferrimagnetic material.

As shown in Fig. 1, Ni has a clearly finite magnetic moment. In order to discuss quantitatively the magnitude of the total magnetic moment ($=\mu^T$) and the contribution of the spin ($=\mu^S$) and the orbital ($=\mu^L$) magnetic moment to the total magnetic moment on Ni atom in $GdNi_2$, we estimate the values of μ^T, μ^L, and μ^S from the MCD spectra by using the magneto-optical sum rules.[7,8] These sum rules could be expressed as follows:

$$\mu^L = \frac{4n_h}{3}\left(\frac{I_{L3}+I_{L2}}{W_{L3}+W_{L2}}\right), \tag{1}$$

$$\mu^S = -n_h\left(\frac{I_{L3}-2I_{L2}}{W_{L3}+W_{L2}}\right)\left(1+\frac{7\langle T_z\rangle}{\langle S_z\rangle}\right)^{-1}, \tag{2}$$

where I_{L3} (I_{L2}) and W_{L3} (W_{L2}) represent the area of the MCD spectrum and the area of the ''white-line'' in the XAS spectrum at the Ni L_3-(L_2-) edge region, respectively; n_h is the hole number in the $3d$ state; and $\langle S_z\rangle$ and $\langle T_z\rangle$ correspond to the expected values of the magnetic dipole matrix operator and the spin operator, respectively. According to Stöhr, $\langle T_z\rangle$ could be equal to zero in the case of polycrystal.[15] Therefore,

$$\mu^S = -n_h\left(\frac{I_{L3}-2I_{L2}}{W_{L3}+W_{L2}}\right) \tag{3}$$

can be obtained. Generally, μ^L/μ^S represented as

$$\frac{\mu^L}{\mu^S} = \frac{4}{3}\left(\frac{I_{L3}+I_{L2}}{I_{L3}-2I_{L2}}\right) \tag{4}$$

is more reliable than the individual values of μ^L and μ^S because it is not necessary to estimate the values of W_{L3}, W_{L2}, and n_h. The ratio of μ^L/μ^S is deduced to be 0.46 from the observed MCD spectrum, which is much larger than 0.095 of Ni metal.[9] According to Manini *et al.*,[11] Ni orbital moment becomes larger when Ni $3d$ holes have an X_2 character. Therefore, we could think that Ni $3d$ holes in $GdNi_2$ have an X_2 character. These results did not conflict the fact that Ni XAS-MCD spectra have satellite peaks when Ni $3d$ holes in $GdNi_2$ have an X_2 character. The value of n_h for the $3d$ state in the $GdNi_2$ system was employed at $n_h=1.59$ by means of the band calculation by Asano and Ishida.[16] Finally, we obtained $\mu^T=0.200(02)\mu_B$, $\mu^L=0.060(01)\mu_B$, and $\mu^S=0.140(01)\mu_B$. These values are consistent with those of other Gd-Ni intermetallic compounds.[6]

Finally, XAS measurement indicated that the $3d$ electronic state, i.e., the $3d$ band, of Ni in $GdNi_2$ is not completely occupied, and XMCD showed that it retains a finite magnetic moment of about $0.2\mu_B$ and an angular momentum component. Furthermore, XMCD revealed that the Ni magnetic moment couples antiparallel to that of the Gd, which is expected from the magnetic structure of heavy RE and $3d$ TM's.[1] These results, which are quite different from the results by Mallik *et al.* and others,[5] suggest that electronic state of the Ni in $GdNi_2$ has a very $3d$ electronic character.

We have measured the MCD in the Ni $2p \rightarrow 3d$ XAS and Gd $3d \rightarrow 4f$ XAS of $GdNi_2$. Clear many-peak structures were observed in both XAS and MCD. The spin and orbital magnetic moments of Ni ions in $GdNi_2$ were deduced to be $\mu^L=0.06\mu_B$ and $\mu^S=0.14\mu_B$, respectively, from the MCD spectra in the Ni $2p \rightarrow 3d$ XAS according to the magneto-optical sum rules. $GdNi_2$ was found to have ferrimagnetism from the sign of the MCD signal. Ni could be considered to have an intrinsic moment even in the Laves phase concentration.

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