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2006 J. Phys.: Condens. Matter 18 6891

(http://iopscience.iop.org/0953-8984/18/29/026)

Institute of Physics Publishing Journal of Physics: Condensed Matter

J. Phys.: Condens. Matter **18** (2006) 6891–6895 doi:10.1088/0953-8984/18/29/026

Detection of Ni magnetic moment in $GdNi_2$ compound by magnetic Compton profile (MCP) method

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Received 2 March 2006, in final form 28 April 2006
Published 6 July 2006
Online at stacks.iop.org/JPhysCM/18/6891

Abstract
The Ni magnetic moment in the $GdNi_2$ Laves phase compound is studied in detail by the use of the magnetic Compton profile (MCP) method. Analysis of the MCP, measured at 30 K, reveals that the spin component of Ni 3d electrons coupled antiparallel to that of Gd 4f electrons, and it was confirmed that the Ni retains a spin magnetic moment of $0.16 \pm 0.08\ \mu_B$. Furthermore, the total magnetic moment, including the angular momentum component, is found to be $0.23 \pm 0.11\ \mu_B$ and this value that is obtained is in accord with that derived from direct measurement of the bulk magnetization. Our finding of the existence of the Ni magnetic moment contradicts the well-known fact that Ni loses its magnetic moment in the Laves phase of rare-earth (RE)–Ni compounds. In addition, the magnetic moment originating from the electrons with s- and p-character, which are donated by the Gd and Ni atoms, is also observed and quantified.

1. Introduction

Rare-earth (RE) transition-metal (TM) compounds and alloys have been one of the most fascinating subjects in magnetism over many decades from the 1950s. At the end of the 1950s, Nesbitt *et al* discovered that the Fe– and Co–Gd systems show ferrimagnetism in the absence of super-exchange interaction through oxygen atoms [1] and since then many various behaviours of magnetism have been discovered in RE–TM systems [2–4]. Furthermore, in the middle of the 1970s, binary RE–TM alloys were found to form amorphous alloys without glass-forming agents, such as boron, carbon and silicon, and since then the amorphous RE–TM alloys have attracted much attention for both their fundamental and applied fields [5]. Since the 1980s,

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the crystalline and non-crystalline RE–TM alloys have been very interesting subjects and vast amounts of data have been accumulated.

As a consequence, some guiding rules and pictures have emerged for understanding the magnetic properties of RE–TM crystalline and non-crystalline alloys. One of these pictures is a charge transfer model [2]. This model describes well the experimental results that the TM magnetic moments decrease gradually with an increase in RE concentration. Based on this model, the electrons belonging to outer shells of RE transfer to the TM and occupy the TM 3d band. It follows that the Fermi level shifts to a higher energy in the 3d density of states (DOS) and consequently the TM magnetic moments decrease gradually with an increase in RE content. As a result, in Ni–Gd systems, whose magnetic structure are the simplest in the RE series, the Ni magnetic moment should decrease, and it vanishes for the RE concentration achieved in the Laves phase of $GdNi_2$. The decrease and the eventual vanishing of the Ni magnetic moment with increasing RE content has been held and accepted in this field [2–4].

However, it is not easy to demonstrate the vanishing of the Ni magnetic moment in $GdNi_2$ from the macroscopic point of view, since the Gd magnetic moment is much larger than that of Ni and dominates the magnetic properties. In addition, there are some exceptional cases where the simple charge transfer model does not describe the experimental results. One example is the amorphous Fe–Gd system, where the Fe retains a constant value of 2 μ_B/atom, irrespective of the contents [6]. That is, there might be a possibility that a magnetic moment of Ni survives even in $GdNi_2$. Based on these scenarios, Yano, Umehara and Sato have undertaken a search for the Ni magnetic moment in $GdNi_2$ and compounds with a richer Gd content (i.e. GdNi) from both the microscopic and the macroscopic points of view. In 1999 and 2000, Yano *et al* carried out a magnetic Compton profile (MCP) measurement [7] and a soft x-ray magnetic circular dichroism (MCD) study on $GdNi_2$ and GdNi compounds [8], with the goal of detecting the Ni magnetic moment which aligns antiparallel to the Gd magnetic moment [2]. However, they could not obtain any decisive results due to some unexpected problems. In 2002, Mizumaki *et al* made a soft x-ray MCD measurement for the $GdNi_2$ Laves phase and succeeded in detecting the Ni magnetic moment which couples antiparallel to that of Gd [9].

In this paper, we have measured the MCP and investigate the electronic states of Ni 3d, Gd 4f electrons and the s- and p-like electrons (that is, 4s and 4p electrons in Ni and 5d and 6s electrons in Gd) in $GdNi_2$ compound in detail and answer the question whether the Ni loses its magnetic moment or not. An MCP measurement has the great advantage that one can clearly separate and extract the component of spin contribution from the 3d and 4f electrons and the free-like electrons (so-called s- and p-like electrons) in the magnetization [10, 11]. We show clear experimental evidence of the 3d Ni magnetic moment. Furthermore, we evaluate the total magnetic moment of Ni (spin and orbital angular momentum) by employing a localized model.

2. Experimental details

The polycrystalline $GdNi_2$ Laves phase was prepared by arc-melting of 99.99% pure Ni and 99.9% pure Gd under a purified argon gas atmosphere. The ingot obtained was annealed for three days at 1170 K and x-ray powder diffraction at room temperature showed reflections that can be indexed by a cubic C15 $MgCu_2$-type crystal structure. The obtained ingot consisted of fairly large single-crystalline grains. The sample used for measurement had a section of 2.8 mm by 2.4 mm and a height of 7.9 mm in order to reduce the demagnetization factor as much as possible.

The MCP measurement was carried out at the AR-NE1 beamline of 6.5 GeV PF-AR of the High Energy Accelerator Research Organization (KEK). Circularly polarized synchrotron radiation x-rays emitted from an elliptical multi-pole wiggler were monochromatized and

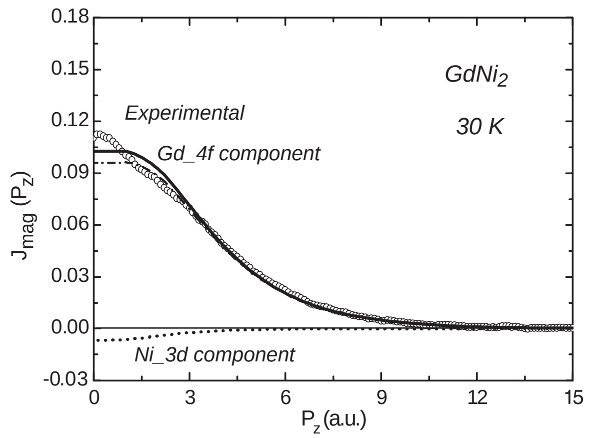

Figure 1. Magnetic Compton profile (MCP) of $GdNi_2$ Laves phase compound at 30 K. Open circles are the experimentally obtained MCP and the solid, dotted and single-dotted lines are the calculated MCPs for Gd-4f, Ni-3d and the subtracted (Gd-4f–Ni-3d) result, respectively. The size of the error bars is as small as the size of circles.

focused on the sample by a single channel-cut bent Si crystal. The energy of the incident x-rays was tuned to 135 keV in order to avoid fluorescences ($K\alpha$ and $K\beta$ from Gd) and we obtained good-quality MCP signals. The energy spectra of Compton scattered x-rays were measured by a solid-state detector (SSD) with 13 Ge elements to achieve high count-rate accumulation. Two energy spectra, I^+ and I^-, were measured repeatedly, where the I^+ and I^- denote that the direction between the sample magnetization and the polarized x-rays is parallel and antiparallel, respectively. By taking the difference $I^+ - I^-$, we can obtain only the spin-dependent Compton scattered component, since the spin-dependent Compton scattering changes its sign on reversing the spin direction, while the charge scattering does not change its sign. In order to change the direction of magnetization of the sample, a superconducting magnet was used. The sample saturated in a field of 0.6 T and a magnetic field of 1 T was employed for the measurement at 30 K. The sample was cooled by a closed-type refrigerator, which enabled us to study the temperature dependence of the MCPs. The MCP data were accumulated over 300 000 counts at peak to obtain data with good-quality statistics.

3. Results and discussion

The MCP for $GdNi_2$ compound at 30 K is shown in figure 1, together with the analysed results. The energy-dependent Compton scattering cross-section, detector efficiency and sample absorption are corrected in the displayed data. The resolution in the z-direction (along the scattering vector) momentum P_Z is 0.5 atomic unit (au). The open circles show the experimental data of MCP and the solid, dotted and single-dotted lines are the analysed data for the Gd 4f, the Ni 3d and the summation of both (i.e. Ni 3d–Gd 4f), respectively. The coupling between the spin components of Ni (TM) and Gd should be antiparallel [2]; in this reference, one can see the diagram of spin orientations, and this ferrimagnetic coupling is illustrated in the figure as the sign (+ and −). The analysis was carried out by fitting the calculated MCP of Gd 4f electrons [12] to the experimental MCP in the momentum region $P_Z \geqslant 5$ au, since, in this sample, the spin component of Gd 4f electrons is expected to dominate, while that of Ni 3d electrons is negligible in this momentum region. From the figure, the calculated MCP for Gd 4f electrons (solid line) can reproduce well the experimental MCP in the region of $P_Z \geqslant 5$ au, however for $P_Z \leqslant 5$ a discrepancy is clearly observed. The measured MCP is smaller than the calculated MCP for Gd 4f electrons in $P_Z \leqslant 5$, and this is evidence that the spin components of some magnetic electrons should couple antiparallel to the spin of Gd 4f electrons. The most likely component of magnetization which couples antiparallel to that of Gd 4f electrons is that of the Ni 3d electrons. Then the calculated MCP of Ni 3d electrons [12], which reproduces well the experimental MCP for Ni metal [13], was used to fit the experimental result, and the obtained MCP for Ni 3d electrons is illustrated in figure 1 as a dotted line in the opposite sign. The MCP that consists of Gd 4f and Ni 3d electrons, which couple antiparallel to each other, is illustrated as a single-dotted line in the figure and reproduces well the experimentally obtained MCP, even in the region $P_Z \geqslant 2$ au. This agreement between data and our model reveals that the Ni does retain an intrinsic spin magnetic moment stemming from 3d electrons in the $GdNi_2$ Laves phase and couples antiparallel to that of Gd 4f electrons. The remaining difference in the region $P_Z \leqslant 2$ au between data and our model is attributed to the so-called s- and p-like electrons belonging to outer shells of Ni (4s, 4p) and Gd (5d and 6s) atoms [13, 14]. The s- and p-like electrons, which are nearly free electrons, contribute in a narrow region of $P_Z \leqslant 2$ au. In principle, the MCPs of s- and p-like electrons stemming from both the Gd and the Ni atoms are mixed and cannot be distinguished clearly. The MCPs of s- and p-like electrons donated from Gd atoms couple parallel to those of the 4f electrons (+ direction in the figure) and those of Ni couple antiparallel to the MCP of 3d electrons of Ni (+ direction) and, as a result, both the MCP of s- and p-like electrons donated from both Gd and Ni atoms orient to the same direction (in the + direction in the figure). After all, it is found that the experimentally obtained MCP consists of three components, that is, the MCPs of Gd 4f electrons, Ni 3d electrons, and s- and p-like electrons donated from Gd and Ni atoms, respectively.

We evaluate the quantitative values of three magnetic moments for 3d (Ni), 4f (Gd), and s- and p-like electrons on the basis that the area of the Compton profile is proportional to the number of electrons, assuming that the area of the 4f MCP corresponds to 7 μ_B/atom. This assumption is reasonable, because the 4f electrons are well known to be localized. From the area of the Gd 4f MCP, we find the spin magnetic moment, that is, the magnetic moment contributed by the spin component of Ni 3d electrons is evaluated to be 0.16 ($\pm$0.08) μ_B and that of s- and p-like electrons of both Gd and Ni atoms is 0.33 ($\pm$0.11) μ_B. Taking account of the experimental result of the soft x-ray magnetic Compton profile [9] and that the MCP detects only the spin magnetic moment, it is neccesary to estimate and amend the angular momentum component to the value of spin contribution. If we employ the ratio of spin magnetic moment to angular (orbital) magnetic moment of 0.43 from soft x-ray MCD (XMCD), the magnetic moment of the angular component becomes 0.07 ($\pm$0.03) μ_B. Finally, we find that the total magnetic moment of Ni is 0.23 ($\pm$0.11) μ_B, by taking into account that the spin magnetic moment couples parallel to angular momentum for more than half of the electrons of Ni in the localized model. On the other hand, regarding the magnetic moment contributed from s- and p-like electrons observed in the region $P_z \leqslant 2$, the division of the s- and p-like component donated from the Gd and Ni atoms cannot be determined uniquely for each atom. Here, if we assume tentatively that the s- and p-like electrons can be divided proportionally to the values of magnetic moments, the value of 0.33 ($\pm$0.04) μ_B for s- and p-like electrons is divided into 0.32 ($\pm$0.03) μ_B/atom for Gd atoms and 0.01 μ_B/atom for Ni atoms. Considering the positive coupling of s- and p-like electrons to the Gd 4f spin magnetic moment and the negative coupling of s- and p-like electrons to the Ni 3d magnetic moment [13, 14], the magnetic moment of Gd becomes 7.32 ($\pm$0.03) μ_B and that of Ni becomes 0.24 ($\pm$0.11) μ_B. The value of 7.32 ($\pm$0.03) μ_B for Gd atoms is a little smaller than that of Gd metal [14] and comparable to that for $Gd_{60}Cu_{40}$ alloy obtained by Tanaka *et al*, who obtained the value of 7.31 μ_B for Gd atoms [15]. On the other hand, the value of 0.24 ($\pm$0.11) μ_B for Ni atoms is a little larger than that obtained by soft x-ray MCD of 0.20 [9] and is in good agreement with the result obtained using macroscopic magnetic measurements (vibrating sample magnetometer), in which the Ni magnetic moment was evaluated from the saturation magnetization at 4.2 K under the assumption of 7 μ_B for the Gd magnetic moment [16]. The value of 0.24 μ_B at 4.2 K obtained using magnetization measurements gives 0.23 μ_B at 30 K from the molecular field analysis.

4. Conclusions

In conclusion, magnetic Compton profile (MCP) measurement revealed clearly that the experimentally obtained MCP for $GdNi_2$ compound is composed of three components, that is, the spin magnetic moments contributed from the Gd 4f electrons, the Ni 3d electrons and the s- and p-like electrons donated from both Gd atoms and Ni atoms. The result that the spin magnetic moment of 3d electrons of Ni couples antiparallel to that of Gd 4f electrons confirms that the Ni retains an intrinsic magnetic moment, stemming from 3d electrons, and this result is in accord with results obtained by soft x-ray MCD and bulk magnetization measurements. This result contradicts the widely held belief that the Ni magnetic moment collapses in the RE–Ni_2 Laves phase, which has been explained by a charge transfer model. Furthermore, the magnetic moment for Ni is estimated to be 0.24 ($\pm$0.11) μ_B at 30 K. This value is larger than that obtained by XMCD by about 20% and is in good agreement with macroscopic measurements.

Acknowledgments

This research was partially supported by a Grant-in Aid for Scientific Research (C). The synchrotron radiation experiment was performed at beamline AR-NE1 of 6.5 GeV PF-AR of the High Energy Accelerator Research Organization (KEK) (Grant No. 2000G169). The authors would like to thank Professor Sakai and Dr Koizumi of the University of Hyogo prefecture, Graduate School of Material Science for their valuable discussions and technical advice. Professor Lovesey of the UK's Rutherford Appleton Laboratory is also deeply appreciated for his careful reading and correction of this manuscript.

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