Magnetic x-ray scattering study of GdCo_2Ge_2 and NdCo_2Ge_2

by

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1 GENERAL INTRODUCTION

Introduction

The results of magnetic x-ray resonant exchange scattering (XRES) experiments are important to the development of an understanding of magnetic interactions in materials. The advantages of high Q resolution, polarization analysis, and the ability to study many different types of materials make it a vital tool in the field of condensed matter physics. Though the concept of XRES was put forth by Platzman and Tzoar[3] in 1970, the technique did not gain much attention until the work of Gibbs and McWhan *et al.* in 1988[4]. Since then, the technique of XRES has grown immensely in use and applicability. Researchers continue to improve upon the procedure and detection capabilities in order to study magnetic materials of all kinds. The XRES technique is particularly well suited to studying the rare earth metals because of the energy range involved. The resonant L edges of these elements fall between 5-10 KeV. Resonant and nonresonant x-ray scattering experiments were performed in order to develop an understanding of the magnetic ordering in GdCo_2Ge_2 and NdCo_2Ge_2 .

Thesis Organization

This work includes a discussion of techniques, bulk magnetic properties, and experimental results from research carried out at Ames Laboratory and the Advanced Photon Source at Argonne National Laboratory. In chapter 2, there is a discussion of the tech-

nique of x-ray resonant exchange scattering. It includes a description of the resonant processes involved along with calculations and references to determine the magnetic cross section of the scattering. There is also a short discussion of nonresonant scattering. Chapter 3 details some of the interesting bulk magnetic properties of materials in the family of RCo_2Ge_2 and also includes more specific information relating to the two compounds of interest: GdCo_2Ge_2 and NdCo_2Ge_2 . A paper that is to be submitted to Phys. Rev. B is included in chapter 4 which discusses the results of an x-ray scattering experiment on a sample of GdCo_2Ge_2 . The modulation vector, moment direction, and ordering temperature were all determined from this measurement as outlined in the chapter. Another experiment is discussed in chapter 5 which details the results of a measurement on a sample of NdCo_2Ge_2 . A modulation wave vector was found and the temperature dependence determined. However, future experiments are needed to determine if this is the only magnetic wave vector present in the sample and to find the orientation of the magnetic moments. Finally, chapter 6 gives general conclusions from the experiments and discusses future research goals.

2 X-RAY RESONANT EXCHANGE SCATTERING (XRES)

Introduction to XRES

XRES involves the study of resonant scattering using incident photons near the absorption edge of a magnetic ion. Photons are absorbed by electrons in the inner shell of a particular ion and result in the excitation of the electron to a higher energy level. In the relaxation process, a photon with equal energy to that absorbed is coherently emitted. The resonance process enhances the intensity of the magnetic satellite peak because the intermediate state is spin-polarized through its interaction with the magnetic f-electrons of rare-earth ions. This allows for peaks with intensities much lower than charge peaks to be detected above background. By adding this enhancement to the high flux that is present in current synchrotron sources, this technique allows for practical measurements of magnetic peaks. X-ray resonant exchange scattering enables the study of magnetic ordering through the determination of wave vectors, ordering temperatures, and magnetic moment directions.

One of the key difficulties in the study of magnetic phenomena using x-rays is that the cross section is smaller than neutron scattering, and x-ray charge scattering, by $(\frac{\hbar\omega}{mc^2})^2 \sim 5 \times 10^{-4}$ counts/second[5]. In a typical neutron experiment, the number of incident neutrons per second is $\sim 10^8$. With modern synchrotron sources, the flux of incident photons can be $\sim 10^{12}$ /sec. This higher incident intensity allows x-ray experiments on magnetic materials to provide results in a similar time frame to neutron diffraction. The scattered intensity does, however, also depend on the size, quality, and composition of

the material. These properties can make one technique better suited for a particular material as will be discussed shortly.

A principal ability of XRES lies in the determination of the magnetic moment directions within the unit cell. By studying the integrated intensity measurement and comparing it with the theoretical cross section, it is possible to determine if the moments are oriented along or perpendicular to particular crystallographic axes.

There are some distinct advantages that XRES has over neutron scattering measurements. An important advantage to the study of magnetism with x-rays is the superior wave vector resolution of an x-ray source. Modern synchrotron sources are capable of angular resolution that is better than neutron diffraction by an order of magnitude [6]. This allows for precise determination of wave vectors as well as the ability to observe minute changes that may indicate magnetic transitions. The comparison of these values for the wave vector with theory is crucial to the understanding of the magnetic interactions involved.

Resonant x-ray scattering also has the advantage of elemental selectivity. One can tune the energy of the incident beam to the absorption edge of an element in a material and study that particular element. Working at the absorption edge, an electronic resonance is found when electrons participate in dipole or quadrupole transitions. Only the photons emitted from transitions in the selected element will contribute to the resonant scattering cross section. If the excited states are sensitive to the magnetization of a sample, then the magnetic moment of the particular ion can be studied. It is also possible to determine that an ion does not possess a strong magnetic moment in a particular compound by the absence of magnetic peaks from such a resonance.

Another strength of magnetic x-ray scattering is that even very small samples can be studied. Small single crystals that have a volume less than the size of the beam can be studied and compared to the theoretical cross section for the projection along the incident beam direction of the entire sample surface. The single crystal is much

more reliable in studying the properties of materials due to the difficulties that arise from the preparation of a powder sample. There is a greater possibility for impurities or strain to be present in the sample when ground into a fine powder. It is also often necessary to produce a large quantity of powder to obtain sufficient scattering with neutron diffraction. The ability to analyze small crystals is particularly helpful when it is difficult to produce large quantities of a pure compound.

Along with very small samples, there are also some samples that are difficult to study with neutron diffraction because of their neutron absorbing properties. These include isotopes of the elements boron, samarium, europium, and gadolinium. It is only possible to study these materials in a neutron diffraction experiment by the use of a sometimes costly isotopic substitution. XRES eliminates the need for this substitution and proves to be a valuable tool for the study of these materials. Due to the importance of gadolinium to the group of rare-earth elements based on its half filled valence band, the technique of XRES must be a vital part of magnetic structure determination for the rare-earths.

The disadvantages of XRES include the fact that there is not yet a defined relationship between the magnitude of the magnetic moment and the intensity of the x-ray resonant peaks. This causes x-ray users to rely on other magnetic measurements for a determination of moment magnitude. The other difficulty of XRES is in the study of ferromagnetic materials. Magnetic peaks that occur at the same position as charge peaks will be lost due to their much lower intensity. A polarization analysis must be employed to study ferromagnets and it is often difficult to extract the resonant peaks from the high charge background. It is much easier to detect satellite peaks that arise from antiferromagnetic ordering. Thus, it is important to use XRES as a complementary technique to neutron scattering in order to determine all of the magnetic properties of a material.

How Does it Work?

The resonant scattering that is studied according to the technique of XRES is a part of the usual anomalous dispersion phenomena[7]. A resonance occurs when the incident photon energy $\hbar\omega = E_2 - E_1$, where E_2 is the excited state and E_1 is the ground state of the electron. When this condition is satisfied, an incident photon can be absorbed by an electron from an inner shell of the element being studied. This electron is excited to an unoccupied state above the Fermi level. Almost instantaneously ($< 10^{-15}s$), the electron will fall back to its ground state and re-emit a photon with equal energy to that absorbed. These photons are coherent and can be collected as an enhancement to the intensity of a magnetic satellite peak. As mentioned before, when a ferromagnetic material is studied, the magnetic peaks will fall on top of the charge peak positions and be indistinguishable. However, for antiferromagnetic materials, the magnetic peaks occur at satellite positions that are centered on a charge peak. The diffraction conditions are different than the charge case since the magnetic ordering does not coincide with the ordering of the lattice. The position of these satellite peaks in relation to the charge peaks in the reciprocal lattice gives the modulation wave vector. This can be determined by measuring the distance from each satellite to the charge peak in reciprocal lattice units.

The origin of the resonance, in most cases, is from electric dipole transitions (E1). This represents a transition from the 2p to 5d shell. In the absence of this resonance, an electric quadrupole transition can be the dominant resonant process. This results in a transition of an electron from the 2p to 4f state. To determine the nature of the resonance involved for a particular compound and reflection, a Q dependent integrated intensity measurement is performed. The measurement of the x-ray cross section for resonant scattering is compared to theoretical predictions for a dipole or quadrupole resonant process to show which resonance more accurately reflects the trend of the

measurement. A preliminary indication of the dominant resonance can be obtained by studying the profile of the intensity of a magnetic peak as the energy is scanned through the resonance. This profile is then compared to the measurement of an absorption curve of a charge peak over the same energy interval. The absorption edge of an element can be determined by finding the position where the fluorescence shows the maximum slope in the absorption. By comparing the position of the peak in the intensity from the resonance with the location of the absorption edge, a suggestion can be made for the nature of the resonance. Fig. 2.1(a) shows the fluorescence of the (0 0 8) charge peak in GdAgSb_2 with the vertical line marking the position of the absorption edge. A signature of a dipole resonance is the location of the peak above the absorption edge as found in plot (c). For a quadrupole resonance, the peak is found below the edge as shown in plot (b). An understanding of the nature of these transitions elucidates the method by which the resonance is probing the magnetization of a sample as will be discussed later.

A strength of XRES is that by tuning the incident energy to an absorption edge of a particular element, it is possible to ascertain that the magnetic scattering observed is from a particular element. This allows one to determine where the moments are located in relation to element positions in the unit cell. It is the excited states that are sensitive to the magnetization density, so the magnetic peaks arise solely from the resonating ion. This elemental specificity also allows for the independent study of different sublattices. It is important to analyze the absorption edges of all magnetic elements in the compound to determine if they carry a moment. With careful study of each elements absorption edge, an x-ray experiment can confirm the nature of the interactions which lead to magnetization in a particular compound.

Sensitivity to Magnetization

The magnetic sensitivity that is obtained from the dipole and quadrupole transitions arises from two different properties of the magnetic ions. For the case of electric dipole - dipole transitions (E1), the transition reflects the exchange splitting of the 5d electron levels resulting in the L_{II} , L_{III} , M_{II} , and M_{III} absorption edges. The magnetic moment associated with the rare earth ions arises from local moments in the 4f orbitals. A direct exchange of the 4f shell with the 5d band leads to an unpaired spin distribution in the 5d shell[1]. This coupling with the 4f shell leads to magnetic sensitivity for the 5d levels. Finally, since the electrons in the 5d band participate in the dipole transition, the resonant intensity depends indirectly on the magnetic ordering of the compound. The electric quadrupole transition, however, involves the electron being excited from the 2p orbital to the unoccupied magnetic 4f “band”. Thus, the electric quadrupole resonance is a direct probe of the 4f magnetization of the ion.

Analyzing Polarization Properties

The polarization of scattered photons can be used to select photons scattered in the resonant process and reduce the background from charge scattering in order to study a sample’s magnetic order. According to the matrix elements that define the amplitude of the resonant scattering, the resonance can lead to a change in polarization between the incident and scattered photons. The effect of the geometry and moment direction on the amplitude of the cross section of x-ray resonant exchange scattering can be written in vector form[8]:

$$f[\varepsilon_f^\dagger, \varepsilon] = \begin{pmatrix} \varepsilon_{\sigma_f}^\dagger \\ \varepsilon_{\pi_f}^\dagger \end{pmatrix}^T \cdot \begin{pmatrix} M_{\sigma \rightarrow \sigma} & M_{\pi \rightarrow \sigma} \\ M_{\sigma \rightarrow \pi} & M_{\pi \rightarrow \pi} \end{pmatrix} \cdot \begin{pmatrix} \varepsilon_\sigma \\ \varepsilon_\pi \end{pmatrix}.$$

The variables are defined according to the labels in Fig. 2.2. From this relation, we can calculate a proportional relation to the overall cross section that will give insight into

the direction of the moments when compared to the integrated intensity measurement.

We begin by defining the incident and scattered polarizations in terms of the scattering angle θ . We have

$$\varepsilon = \varepsilon_\sigma \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix} + \varepsilon_\pi \begin{pmatrix} \sin \theta \\ 0 \\ \cos \theta \end{pmatrix}$$

and

$$\varepsilon_f = \varepsilon_\sigma \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix} + \varepsilon_\pi \begin{pmatrix} -\sin \theta \\ 0 \\ \cos \theta \end{pmatrix}.$$

The relation $|\varepsilon_\sigma|^2 + |\varepsilon_\pi|^2 = 1$ must always hold. The incident and scattered momentum vectors can be represented in terms of θ as well:

$$\hat{k}_i = \begin{pmatrix} \cos \theta \\ 0 \\ -\sin \theta \end{pmatrix}$$

and

$$\hat{k}_f = \begin{pmatrix} \cos \theta \\ 0 \\ \sin \theta \end{pmatrix}.$$

The matrix elements M are functions of $(\varepsilon_f^\dagger \times \varepsilon) \cdot \hat{z}$ where $\hat{z}$ is the vector representing the moment direction. The elements can be calculated as follows:

$$M_{\sigma \rightarrow \sigma} = 0$$

$$M_{\sigma \rightarrow \pi} = -\hat{k}_f \cdot \hat{z}$$

$$M_{\pi \rightarrow \sigma} = \hat{k}_i \cdot \hat{z}$$

$$M_{\pi \rightarrow \pi} = (\hat{k}_f \times \hat{k}_i) \cdot \hat{z}$$

Thus, we have

$$M = \begin{pmatrix} 0 & z_1 \cos \theta - z_3 \sin \theta \\ -z_1 \cos \theta - z_3 \sin \theta & z_2 \sin 2\theta \end{pmatrix}$$

The incident beam from the synchrotron source is mainly σ polarized. Since the $\sigma \rightarrow \sigma$ scattering is not a part of the resonant process for dipole transitions, we can use an analyzer in the scattered beam to suppress the charge scattering and look at mainly π polarized photons. Using a pyrolytic graphite (PG) analyzer with a 0.5 degree mosaic, the π polarized component of the scattered beam can be studied independently. Using the PG(006) reflection, the beam is scattered at an angle of $2\theta \approx 100$ degrees for $E = 7.243\text{KeV}$ (Gd L_{III} edge). The σ polarized component is suppressed since its polarization vector is nearly parallel to the direction of propagation of the photons[1].

Another benefit of polarization analysis is that the higher intensity charge scattering is not seen in the π polarized scattering. Thus, working in the $\sigma \rightarrow \pi$ geometry greatly decreases the overall background. This enables the study of very weak magnetic peaks such as those which arise from higher harmonics associated with a modulation of moments. There will be more discussion of this later in dealing with GdCo_2Ge_2 .

When the magnetic moment is not in the scattering plane, or in a nonresonant experiment, it is important to use the PG(002) reflection to study both σ and π components of the scattered beam. This analyzer scatters at a smaller angle which allows both polarizations to be detected. Including this configuration in an experiment allows all components of the magnetic moment to be studied without reorienting the sample.

Determination of the Moment Direction

In order to determine the direction of the magnetic moments, it is necessary to measure the integrated intensity of the scattering. This is done by opening the detector slits to allow all of the scattered photons to be detected as a transverse scan is carried out. This measurement allows for the comparison of the full intensity from peaks at different positions in the reciprocal lattice. The theoretical cross section has been calculated for this geometry with the $(h0\ell)$ zone in the scattering plane[8]. The integrated intensity in

the $\sigma \rightarrow \pi$ geometry for a dipole resonant process can be written as

$$I = A \frac{(S_3 \sin(\theta) - S_1 \cos(\theta))^2}{\sin(2\theta)}$$

where $\frac{1}{\sin(2\theta)}$ is the Lorentz polarization factor[9]. The variables S_3 and S_1 are the components of the magnetic moment in the 'c' and 'a' crystallographic directions, respectively, for a particular orientation of the sample. The component of the moment along the 'b' direction, S_2 , does not play a role because it is directed out of the scattering plane. Only moments in the scattering plane can contribute to the resonant scattering. This is complicated by the presence of multiple domains and the nature of the tetragonal unit cell that makes the 'a' and 'b' directions identical. The geometry prohibits the precise determination of the magnetic moment direction along the a-, b-axis, or at an angle between them. If the magnetic transition was accompanied by a structural tetragonal-to-orthorhombic phase transition as in the case of $\text{TbNi}_2\text{B}_2\text{C}$, then the moment direction could be determined precisely[10]. But in the absence of this structural transition, the only clear determination that can be made is whether the moments are parallel or perpendicular to the c-axis.

Nonresonant scattering can also give important information about the orientation of the magnetic moments. The relative intensity of these peaks to the background is much lower than the resonant scattering, however, for detectable magnetic peaks, the results can still be compared to the theoretical cross sections. For nonresonant scattering in the $\sigma \rightarrow \sigma$ geometry, the magnetic scattering is particularly sensitive to the moments directed out of the scattering plane. For this measurement, the energy is tuned to a value far from the absorption edge. Using the same convention as shown in Fig. 2.2, the matrix M can be written as

$$M = \begin{pmatrix} S_2(\sin 2\theta) & -2(\sin^2 \theta)[(\cos \theta)(L_1 + S_1) - S_3(\sin \theta)] \\ 2(\sin^2 \theta)[(\cos \theta)(L_1 + S_1) + S_3(\sin \theta)] & (\sin 2\theta)[2(\sin^2 \theta)L_2 + S_2] \end{pmatrix} [11].$$

This leads to an intensity which scales according to

$$I \propto |f_{mag}(Q)|^2 \frac{1}{\sin 2\theta} \cdot (S_2^2 \sin^2 2\theta + 4 \sin^4 \theta \cdot (S_1 \sin \theta + S_3 \cos \theta)^2).$$

A comparison of the integrated intensity in the nonresonant configuration with the equation above helps confirm the direction of the moments in the unit cell as will be shown for the case of GdCo_2Ge_2 in chapter 4.

Figure 2.1 Energy profiles near the Gd L_{III} edge for $GdAgSb_2$. (a) The fluorescence from the $(0\ 0\ 8)$ peak is shown. (b) The resonant scattering enhancement at the $(\frac{1}{2}\ 0\ 8)$ magnetic satellite peak occurs before the edge indicating a quadrupole resonance. (c) The resonant enhancement at the $(0\ -\frac{1}{2}\ 8)$ magnetic satellite peak occurs above the edge suggesting a dipole resonance. Intensities are similar due to a change in the analyzer angle. Studied by C. Song *et al.* [1, 2]

Figure 2.2 Diagram of experimental set-up showing incident photon with momentum $\hat{k}_i$ and scattered photon $\hat{k}_f$ and the $(h\ 0\ \ell)$ scattering plane.

3 THE RCo_2Ge_2 SERIES

Introduction

In order to understand the magnetic properties of a material, it is important to study the background of similar materials and determine the interactions that lead to magnetic order. The RCo_2Ge_2 compounds belong to the series RM_2X_2 , where R is a rare earth element, M is a transition metal, and X is either Ge or Si. These compounds have been extensively studied in the literature [12]. In each series, the structure, susceptibility, neutron cross section, and Mossbauer spectra have been determined for many of the compounds. This series also includes the RNi_2Ge_2 compounds that have been found to exhibit strong Fermi surface nesting which leads to the magnetic ordering[6]. The many similarities between RNi_2Ge_2 and RCo_2Ge_2 suggest that Fermi surface nesting may also be the source of magnetic order in these compounds. The compounds can order either ferromagnetically or antiferromagnetically depending on the transition metal[13]. Though many of the compounds in the RCo_2Ge_2 series order in a simple antiferromagnetic structure of type I, there are anomalies which have been reported to undergo multiple transitions such as NdCo_2Ge_2 [14]. There are other interesting members of the series as well. A surprising result was found in a comparison between the compounds EuCo_2Ge_2 and GdCo_2Ge_2 . The europium ion is divalent and the gadolinium ion is trivalent. This leads to identical ground states, but it has been reported[15] that these compounds have a very different magnetic state. For most members of the series, the exchange interaction can be described in terms of the Ruderman-Kittel-Kasuya-Yosida

(RKKY) model and the effects of the crystal electric field (CEF) which determine the magnetic ordering. The exceptions are the gadolinium and europium compounds in which CEF effects are minimal. In this chapter, the physical properties common to the series and the interactions that affect the magnetic ordering will be discussed.

Physical Properties

Many compounds in the family of RM_2X_2 , including all the RCO_2Ge_2 compounds crystallize in the $ThCr_2Si_2$ type structure ($I4/mmm$). This is a tetragonal structure and each unit cell contains two formula units. The atoms are located according to these site positions: R on 2(a), M on 4(d), and X on 4(e) sites[15]. The locations of these ions are very important to the magnetic ordering due to the interactions involved. The moment resides mainly on the rare-earth site and it is the interaction between the rare-earth ions that is most important. As long as the transition metal M has no moment, the R-R distances play an important role in the interaction [15]. There has also been a suggestion that the Néel temperature depends on interlayer distances [16]. This prediction comes from the fact that the transition temperatures were found to be lower for germanides than in the case of silicides. The large c/a ratio for the series, close to 2.5, suggests that there may be large anisotropies present in the physical properties of the material[17].

Another physical property of the series relates to the lattice parameters and unit cell volume. The series undergoes the usual lanthanide contraction as the atomic number is increased through the elements. The only exception to this is $YbCo_2Ge_2$ which can be accounted for by assuming that the ytterbium is in the divalent state as magnetic susceptibility measurements suggest[12].

Magnetic Structure

The magnetic structure of most compounds in the series of RCo_2Ge_2 is simple antiferromagnetic of type I. This can be described as an antiferromagnetic stacking of ferromagnetic sheets perpendicular to the c -axis. The stacking forms an antiferromagnetic sequence of $+ - + - \dots$ along the c -axis and leads to a modulation vector in this direction[17]. It has been proposed that strong anisotropic exchange interactions may be the cause of this layered magnetic structure [17]. This can be understood by looking at the c/a ratio. The rare-earths are much farther apart along the c -axis than in the tetragonal basal plane. It has also been shown by neutron studies that the moments are highly localized on R^{3+} ions [17]. Thus, there is not any overlap of orbitals between neighboring ions. The interaction must be indirect via the electrons in the conduction band.

In order to determine the ordering temperatures of different compounds in the series, extensive susceptibility measurements have been carried out [13, 16, 17, 18, 19]. The compounds in the series of RCo_2Ge_2 typically show a peak in the susceptibility measurement between 6 and 46K. This local maximum generally indicates the transition to an ordered magnetic state. In most compounds of the series, this state is one of antiferromagnetism. For the two compounds discussed at length in this thesis, susceptibility measurements were reported showing a magnetic transition for GdCo_2Ge_2 near 40 K and for NdCo_2Ge_2 two transitions were reported at 28 K and 13 K[13].

Another interesting question relating to the ordering temperatures is the paramagnetic susceptibility above T_N . This can be described by a Curie-Weiss form with a temperature independent term added. The susceptibility is

$$\chi_M = \chi_{0,M} + \frac{C_M}{T - \theta},$$

where χ_M is the molar susceptibility, $\chi_{0,M}$ is the temperature independent term, C_M is the Curie-constant, T is the temperature, and θ is the Weiss constant[13].

In the series of RCo_2Ge_2 compounds, the moments are highly localized on the rare-earth (R^{3+}) ion for most members of the series. However, for the case of EuCo_2Ge_2 , the europium ion is divalent, and it was reported that there is also a moment on the cobalt atom for the powder sample studied[15]. It was not clear if this cobalt moment orders independently of the rare-earth ions or at what temperature the transition to magnetic order occurs. The presence of the cobalt moment has also not been confirmed in a single-crystal experiment.

Assuming that the results of the powder experiment are correct, an interesting comparison can be made with the gadolinium member of the series. The europium ion is divalent and hence has the identical ground state to the trivalent gadolinium ($4f^7, {}^8S_{7/2}$). However, when these ions are present in the compound RCo_2Ge_2 , there is a moment found on the cobalt ion only in the europium case. A suggestion for the origin of the moment on the cobalt ion is that it is allowed by the divalent nature of the europium ion. This was predicted due to a study of the compound EuCo_2GeSi [15]. When there is a substitution of silicon for one of the germanium ions, it is found that 26% of the europium ions are trivalent based on Mossbauer spectra measurements[15]. In this case, the cobalt is found to carry no moment. Thus, it was proposed that the presence of the extra conduction electron in the trivalent state eliminates the magnetic moment from the cobalt positions in GdCo_2Ge_2 .

An x-ray experiment on EuCo_2Ge_2 could provide insight into the presence of the cobalt moment, but there are several problems with this measurement that may make it difficult to determine. As mentioned before, in order to observe magnetic peaks above a much larger electronic peak background, it is necessary to tune the incident beam to the energy of a resonance for the element in question. The most common resonances that are studied are the L_{II} and L_{III} edges. For the case of cobalt, these energies are too low to probe all of reciprocal space in the sample. Only small wavevectors near the origin could be detected. The energy of the K edges for cobalt are much more reasonable, but the

resonance here involves transitions between s and p states. The magnetic moments for cobalt arise in the d electron shell and the coupling of the d electrons to the p electrons is very weak. Thus, the magnetic structure will be only weakly displayed in the K edge resonance making it difficult to detect. Therefore, an x-ray measurement has the ability to find the cobalt moment if it is close to the origin of reciprocal space or if it is quite strong. However, if it is not found in such an experiment, it will be difficult to say with certainty that it is not present at all. It could just as well be present in a signal that is below the background and cannot be observed.

Theory of Magnetism in RCo_2Ge_2

With its tetragonal structure, the easy axis of magnetization in RCo_2Ge_2 can be found relative to the unique (001), (100), or (110) axis. This angle is determined by the position of lowest free energy for the system[15]. There are two main interactions that can affect magnetic ordering in this system. The RKKY indirect exchange interaction takes place via conduction electrons and, in some cases, leads to antiferromagnetic ordering. The crystalline electric field can also affect the magnetic ordering and leads to anisotropic behavior of the magnetization. It is the combination of these two interactions that gives the overall magnetic structure of a compound.

Evidence that the conduction electrons are the cause of the exchange interaction can be found in the low temperatures of the phase transitions and the large rare-earth - rare-earth distances [16]. These properties suggest that the interaction is RKKY in nature. For a simple case of the RKKY interaction, the compounds should order antiferromagnetically with the Néel temperatures scaling according to the de Gennes function. This is the case for many of the heavy rare-earth compounds. However, the lighter rare-earths in RCo_2Ge_2 compounds do not scale according to the de Gennes function[16]. This indicates that the assumptions of de Gennes scaling may break down

for these compounds. It is possible that the conduction electron density, $N(E_F)$, or the conduction-electron R-ion exchange coupling parameter, I , may vary in the relation $T_N \sim N(E_F)I^2(g-1)^2J(J+1)$. Another interaction is suggested by similarities of the series to the extensively studied RNi_2Ge_2 [6]. In this series, it was found that the magnetic ordering is due to RKKY and CEF effects with a strong dependence on Fermi Surface Nesting. It appears that the crystal field anisotropies have an important effect on the magnetic ordering in the series RCo_2Ge_2 as well.

RKKY and Crystal Field Anisotropy

RKKY is an indirect exchange interaction that occurs via the spin polarization of the conduction band [20, 21, 22, 23]. Since the 4f electrons are highly localized on the rare-earth atoms, there is no overlap of the electron orbitals that would result in a direct interaction. Thus, the dominant interaction is indirect through the exchange of spin polarized electrons in the conduction band. The presence of a local magnetic moment on an ion site causes the polarization of the conduction electrons in this region. This leads to an oscillating magnetic field which emanates to neighboring ions. The field affects the local magnetic moment of the neighbors and, hence, sets up the interaction[1].

Magnetic anisotropy is another important contribution to magnetic ordering. The layered magnetic structure discussed earlier is the result of strong anisotropic exchange interactions[17]. The exchange interaction within the (001) planes is found to be strongly ferromagnetic, while the coupling that is present between neighboring planes along the c-axis is weaker and often antiferromagnetic [17]. This leads to moments ordering parallel to nearest neighbors in the plane and antiparallel to moments in neighboring planes. An indication of the presence of strong magnetocrystalline anisotropy is the fact that the moments do not reach saturation even at 50 kOe and $T = 4.2$ K for a powder sample[16]. With powder samples, however, it is difficult to distinguish anisotropy due

to averaging over all lattice directions. Other techniques can be used to characterize the magnetic anisotropy. In order to determine the microscopic magnetic anisotropy for a certain rare earth intermetallic, the Mossbauer spectra can be measured[24]. A large uniaxial anisotropy is found in the measurement of the high field susceptibility[17]. The orientation of the moments in many of the compounds appear to be either perpendicular or parallel to the c-axis due to this uniaxial anisotropy.

The magnetic anisotropy, present in some members of the series due to the point symmetry of the rare earth site, indicates the possibility for a detailed study of spin glasses. This anisotropy leads to an Ising spin state that can be compared to theoretical calculations. An ion that satisfies the Kramer criterion and has a high degree of magnetic anisotropy at low temperatures may be a good candidate to create a glassy state. Based on previous studies of the properties of certain elements, candidates for this include NdCo_2Ge_2 and DyCo_2Ge_2 .

The anisotropy of the series of RCo_2Ge_2 points to the importance of crystal field theory to the interactions. It has been noted, earlier in this work, that with the exception of gadolinium and europium, the compounds have competing interactions between the crystal field and the RKKY interactions. The crystal field effects result from the electromagnetic interactions of ions within a crystal structure. These fields lead to a splitting of the once degenerate Zeeman levels found in an unfilled shell of a free ion[8]. In the crystal, the symmetry of the ion's location in the lattice, coupled with the shape of the exchange split orbitals, determines the extent of the effect of the crystal field on the magnetic ordering of a sample. According to the theory for the case of a magnetic ion at a position of tetragonal point symmetry, the CEF energy can be written as

$$H_{CEF} = B_2^0 O_2^0 + B_4^0 O_4^0 + B_4^4 O_4^4 + B_6^0 O_6^0 + B_6^4 O_6^4,$$

where B_n^m are the CEF parameters that determine the scale of the splitting[25]. The orbitals are generally not spherically symmetric which leads to the anisotropies in the

crystal field with respect to different ions and lattice directions. However, some rare-earth elements, namely gadolinium and europium, have a half filled 4f shell. This leads to zero angular momentum for the orbitals and a symmetric interaction of the crystal field with the environment surrounding the ions. There is no exchange splitting of the energy levels in this case, so the only interaction that must be considered with regard to magnetic ordering is the RKKY interaction. A more complete discussion of CEF theory can be found in the literature[8, 25].

Moment Size and Orientation

The measured values of the effective magnetic moments, extrapolated from paramagnetic measurements above T_N , for compounds in the series RCo_2Ge_2 are close to the theoretical predictions for free rare-earth ions[16]. This suggests that the magnetic moment arises mainly from the rare-earth atom with only a small contribution from the moments on the conduction electrons. The main contribution to magnetic ordering from the rare-earth ions appears to be true for all trivalent ions in the series.

The principle goals of this paper include a high resolution measurement of the wave vector, the determination of the orientation of the moments in the unit cell, and a precise measurement of the ordering temperatures for the compounds GdCo_2Ge_2 and NdCo_2Ge_2 . Previous proposals have been made as to the orientation of moments from measurements of neutron and Mossbauer experiments [14, 15]. Due to the high opacity of europium and gadolinium to neutrons, neutron scattering has not been employed for the study of these particular rare-earth compounds. ^{151}Gd Mossbauer measurements of GdCo_2Ge_2 have shown that the quadrupole interaction is very different at 77 K as compared to 4.1 K indicating the presence of magnetic ordering[15]. Using this technique it is possible to make a prediction of the angle θ between the magnetic hyperfine field and the c-axis. The angle determines the direction for the easy axis of magnetization and can be

measured for each of these compounds[15]. Other elements of the series for which there have been moment orientation predictions include praseodymium, neodymium, terbium, dysprosium, and holmium, which all have moments parallel to the c-axis [13, 17].

In the case of GdCo_2Ge_2 , a possible moment direction has been proposed according to the results of previous experiments and the theoretical assumption that the exchange interaction is entirely RKKY. The lack of CEF effects makes this compound unique in the series. It can be thought of as a standard by which the influence of the crystal electric field can be determined in other compounds of the series. According to ^{155}Gd Mossbauer spectra, the moments in GdCo_2Ge_2 appear to have an angle $\theta \approx 90$ degrees from the c-axis[15, 24]. This suggests that the magnetic moment is oriented in the basal plane of the tetragonal unit cell with very little component along the c-axis. This can be compared to the results of an x-ray resonant exchange scattering experiment discussed in chapter 4 which confirms the moment direction.

For the case of NdCo_2Ge_2 , neutron and susceptibility measurements have been performed that report a magnetic ordering wave vector, temperature, and predictions of moment directions [13, 16, 17]. According to susceptibility measurements, NdCo_2Ge_2 appears to have two transitions. There are peaks in the susceptibility at temperatures of 28 K and 13 K[13]. From 10-28.5 K, a modulated structure is reported with $k_z = 0.75$ r.l.u. which explains the peak in the susceptibility at 28 K as the Néel temperature. This result is similar to a report from neutron scattering measurements on powder samples which shows an ordering wave vector between 10-26.5 K as $k = (0, 0, 1 - k_z)$ where $k_z = 0.261$ r.l.u.[14]. It was proposed that the crystal electric field may lead to a second transition between 10-13 K resulting in the second peak in the susceptibility [13]. It was predicted that below ~ 10 K a collinear AF structure of type I exists[17]. Neutron measurements report a commensurate AF structure below 12 K with wave vector $k = (0, 0, 1)$ which coexists with the incommensurate structure reported above [14]. In order to confirm the magnetic structure of NdCo_2Ge_2 at low temperature which was reported for

a powder sample, a resonant x-ray experiment on a single-crystal sample was performed and is discussed in chapter 5.

4 MAGNETIC X-RAY SCATTERING STUDY OF GdCo_2Ge_2

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Abstract

A magnetic x-ray scattering study was performed in order to determine the magnetic structure of GdCo_2Ge_2 . The naturally abundant Gd isotope is highly opaque to neutrons which makes the use of magnetic x-ray scattering important. This compound orders in an incommensurate antiferromagnetic (AF) structure characterized by a propagation wave vector $\tau = (0 \ 0 \ \tau_z)$. The value of τ_z is temperature dependent and approaches $0.932(\pm 0.002)$ r.l.u. below $T_N = 32.9\text{K}$. A peak corresponding to 3τ was also observed at $T = 6\text{K}$ indicating the squaring up of the magnetic structure as temperature decreases. Resonant measurements were performed at the L_{III} edge of Gd in a σ to π geometry that is particularly sensitive to resonant dipole scattering. Nonresonant measurements were carried out 250 eV below the edge to study the contribution of moments out of the scattering plane. Fitting the Q dependence of the integrated intensities to a dipole resonant process indicates a moment direction perpendicular to the c-axis. Nonresonant measurements confirm that the moment direction is in the tetragonal basal plane.

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Introduction

The properties leading to magnetic ordering among the system of compounds RCo_2Ge_2 , where R is a rare-earth element, can be studied individually to determine their influence. It is clear that a major contribution to the magnetic ordering for the entire series is the Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction. However, by interchanging the rare-earth ion, varying degrees of anisotropy develop and crystalline electric field (CEF) effects come into play. NdCo_2Ge_2 and DyCo_2Ge_2 are two examples of compounds which possess a high degree of anisotropy. This makes these materials good candidates for detailed spin glass studies. In order to study the anisotropy and CEF effects, it is necessary to have a control compound that exemplifies the magnetic state in their absence. Gadolinium ions have negligible single ion anisotropy and with the 4f orbitals in a state of zero angular momentum, the CEF effects in GdCo_2Ge_2 are minimal. In this compound, it is primarily the RKKY interaction that determines the ordering. Careful study of the ordering wave vector provides information about the nature of both of the interactions on the magnetic ordering. It is necessary to determine the wave vector for GdCo_2Ge_2 to provide a starting point for defining the collective behavior of the magnetic moments in the absence of CEF effects.

Sample

The compounds RCo_2Ge_2 all crystallize in the body centered tetragonal ThCr_2Si_2 -type structure (space group $I4/mmm$)[12]. Typical magnetic modulation wave vectors for these compounds are $(0\ 0\ \tau_z)$ with τ_z between 0.7 and 1.0. These estimates are based on neutron results from other members of the family including NdCo_2Ge_2 which has a wave vector of $(0\ 0\ 0.739)$ [14]. While many members of this family of compounds have been investigated through neutron scattering studies, the magnetic structure of GdCo_2Ge_2 has not been determined. This is most likely due to the neutron opacity of

naturally occurring gadolinium. Resonant magnetic x-ray scattering provides an alternative to neutron measurements in these cases.

Single crystals were grown at the Ames Laboratory using a high temperature flux growth technique[26, 27]. The crystals form as platelets with the unique c-axis perpendicular to the surface. The specimen with the smoothest surface, without visible flux inclusions, was chosen for the x-ray experiment. It was characterized on a four circle diffractometer using a rotating anode (Mo) x-ray source. The sample mosaic was measured to be 0.012 degree at the (0 0 8) reflection. Susceptibility measurements performed at Ames Laboratory using a SQUID magnetometer exhibit a peak at $T_N = 33\text{K}$ as seen in Fig. 4.1. By studying the typical divergence of the susceptibility below T_N with the field applied along or perpendicular to the c-axis, a prediction can be made for the moment direction in the sample. From the figure, it is clear that the susceptibility with the field along the c-axis is nearly flat for temperatures below the transition, while the susceptibility with the field perpendicular to c decreases. This behavior indicates that the moments may lie in the tetragonal basal plane perpendicular to the c-axis. It is necessary to measure the resonant and nonresonant x-ray scattering cross sections and compare with theory to confirm the moment direction.

As mentioned before, the major factor contributing to the magnetic ordering is the RKKY exchange interaction between the moments on the gadolinium ions. RKKY is an indirect interaction that is mediated by conduction electrons[20, 21, 22, 23]. The conduction electron spins are polarized by the presence of a local magnetic moment. The polarized conduction electrons produce an oscillating magnetic interaction that alters the local magnetic coupling of other ions[1]. It is this indirect interaction that leads to antiferromagnetic ordering of the gadolinium moments.

Figure 4.1 SQUID susceptibility measurements with field $H = 1$ kOe applied along the (001) or (100) direction. Peak is at about 33 K.

Experiment

The x-ray experiment was carried out at the MUCAT (Sector 6(ID)) beamline of the Advanced Photon Source (APS). A liquid nitrogen cooled, double bounce Si(111) monochromator and a bent mirror were used to select an energy, focus the beam, and suppress higher-order harmonics. The sample was mounted on a copper rod in the cold finger of a closed cycle displacer. The sample, oriented so that the scattering plane was coincident with the (h0l) zone, was encapsulated in a Be dome with a He exchange gas to enhance thermal stabilization.

Most experiments were carried out near the L_{III} absorption edge of gadolinium ($E = 7.243$ KeV) with a σ -polarized source of incident radiation. In this geometry, only the component of the magnetic moment that is in the scattering plane (a_c) will contribute to

the resonant scattering[1]. A pyrolytic graphite analyzer PG(0 0 6) was used to reduce the background from charge scattering. The analyzer is positioned on the detector arm of the diffractometer and scatters the radiation by nearly 100 degrees in two theta for $E=7.243$ KeV. The final direction of propagation is nearly coincident with σ polarization of the scattered photons. This effectively suppresses $\sigma \rightarrow \sigma$ scattering by $\sim 97\%$ while allowing nearly all of the $\sigma \rightarrow \pi$ scattering to be detected. The dipole resonant process, involved at the L_{III} edge of gadolinium, contributes to the π scattered radiation which enhances the intensity and enables the detection of magnetic peaks[9, 11].

Results

Based on previous results from compounds in the RCo_2Ge_2 series, a search was carried out for a modulation wave vector of the form $(0\ 0\ \tau_z)$ with τ_z between 0.7 and 1.0. Magnetic peaks were found corresponding to $(0\ 0\ L\pm\tau_z)$, where L is an even integer. The reciprocal lattice peak position was found to be temperature dependent and have a value of $\tau_z = 0.932(\pm 0.002)$ r.l.u. Fig. 4.2 shows a plot of the temperature dependence of the wave vector as determined from a fitting to the integrated intensity measurement of the $(0\ 0\ 8-\tau_z)$ satellite peak position subtracted from the position of the $(0\ 0\ 8)$ charge peak. The scattered radiation was measured with wide open detector slits and fit with a Lorentzian peak profile to determine the integrated intensity. The continuous change in the wave vector with temperature is indicative of the incommensurate nature of the AF state. The wave vector grows as temperature is increased to reach a maximum of 0.934 r.l.u. at $T=25$ K and then decreases as the temperature approaches T_N .

The magnetic peaks decrease in intensity and disappear when the thermal energy overcomes the RKKY exchange energy at $T_N \approx 33$ K as shown in Fig. 4.3. In order to develop an understanding of the resonant process, energy scans through the L_{III} edge of gadolinium were performed and are shown in Fig. 4.4. The absorption edge, defined by

Figure 4.2 Temperature dependence of the wave vector in reciprocal space measured in relation to the (008) peak position using the (0 0 8- τ) satellite. The continuous change of the wave vector with temperature is indicative of the incommensurate nature of the AF state.

the maximum slope in absorption, is shown in the figure as the dotted vertical line[8]. The position of the resonant peak above the edge indicates that the transitions are dipole in nature[1].

A measurement of the order parameter for the antiferromagnetic transition was performed and is plotted in Fig. 4.5. A fit using $I = A(T_N - T)^{2\beta}$ is drawn to determine an accurate value for T_N . The intensity of the magnetic peak goes to zero at $32.9(\pm 0.2)$ K according to the fitting with $\beta = 0.26(\pm 0.01)$. This is consistent with the susceptibility measurements which show a transition at 33K.

A search for the 3τ reflection resulted in a peak that was temperature dependent and disappeared into the background below T_N . In the inset of Fig. 4.5, the intensity of this peak is plotted along with the theoretical fit using $I = A(T_N - T)^{6\beta}$. The presence of higher order harmonics of the magnetic ordering indicates a squaring up of the modulation as the temperature is decreased below T_N .

Figure 4.3 Scans along the L reciprocal space direction showing the appearance and increase in intensity of the $(0\ 0\ 8-\tau_z)$ peak as the temperature is lowered.

To determine the direction of the magnetic moments, the integrated intensity was measured at all peak positions corresponding to $(0\ 0\ L\pm\tau_z)$ that could be reached in this geometry. The integrated intensity at each peak is shown in Fig. 4.6 along with theoretical curves for the magnetic moment direction for dipole resonant scattering. The integrated intensity in the $\sigma \rightarrow \pi$ geometry for a dipole resonant process can be written as

$$I = A \frac{(S_3 \sin(\theta) - S_1 \cos(\theta))^2}{\sin(2\theta)},$$

where $\frac{1}{\sin(2\theta)}$ is the Lorentz polarization factor, S_3 and S_1 are the magnitudes of the moments along the c - or a -axis, respectively, for a particular sample orientation, and

Figure 4.4 Energy scans of the (a) scattered intensity at the $(0\ 0\ 8)$ peak position and (b) resonance at the $(0\ 0\ 8-\tau_z)$ satellite peak position. The dotted line marks the position of the absorption edge of Gd.

θ is the scattering angle[9]. For the moment direction entirely along the c -axis, $S_1 = 0$ and the resulting equation describes the dashed line in Fig. 4.6. For the moment direction perpendicular to the c -axis, the theoretical scaling is shown by the solid line. With the exception of the two points at extremely low angles, the data fits very well with the solid line. The discrepancy at low angles can be attributed to the sample not intercepting the entire beam. The beam size was $0.4(\pm 0.03)\text{mm} \times 1(\pm 0.03)\text{mm}$ and the sample was about $3\text{mm} \times 3\text{mm}$. Thus, only half of the predicted intensity is measured at low angles. For all measurements above $\theta = 8$ degrees, the sample intercepted the whole beam allowing for a consistent incident intensity measurement. Due to the domain structure of the tetragonal sample and the nature of the modulation along the c -axis, it is not possible to distinguish the moment directions parallel to the a - or b -axis. Thus, we conclude that the moments are in the (ab) plane of the tetragonal unit cell.

In order to confirm the direction of the moments, a nonresonant scattering measure-

Figure 4.5 Order parameter measurement to determine the transition temperature. Solid line is a fit using $I = A(T_N - T)^{2\beta}$. The inset is a measurement of the 3τ peak.

ment was carried out at an energy of 7 KeV. This is ~ 250 eV below the resonant edge which ensures that the resonant scattering does not contribute to the integrated intensity. The results of the Q dependence are plotted in Fig. 4.7 along with the theoretical curves for nonresonant scattering. The measurement was taken in the $\sigma \rightarrow \sigma$ & π geometry. This decreases the ratio of the intensity of magnetic peaks to background, but it allows all components of the magnetic moment to contribute to the scattered intensity. This configuration is particularly sensitive to the moments that are out of the scattering plane. Thus, by comparison with resonant results, the contribution of all moment directions can be determined without realignment of the sample. As seen in Fig. 4.7, the nonresonant measurement confirms that the moments lie in the basal plane of the tetragonal unit cell.

In conclusion, the compound GdCo_2Ge_2 orders antiferromagnetically below a tran-

Figure 4.6 Q dependence of the integrated intensity. The solid line represents the theoretical prediction for moments aligned perpendicular to the c-axis. The dotted line represents moments aligned along the c-axis.

sition temperature of $T_N = 32.9(\pm 0.2)K$. The modulation wave vector was found to be $(0\ 0\ \tau_z)$ where $\tau_z = 0.932(\pm 0.002)$ r.l.u. Careful comparison of results with theory indicates a moment direction perpendicular to the c-axis.

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Figure 4.7 Nonresonant Q dependence of the integrated intensity. The solid line represents moments aligned perpendicular to the c -axis. The dotted line represents moments aligned parallel to c .

5 RESONANT MAGNETIC X-RAY STUDY OF NdCo_2Ge_2

Overview

A particularly interesting compound in the RCo_2Ge_2 family is NdCo_2Ge_2 . This compound exhibits two peaks in susceptibility measurements that seem to indicate multiple magnetic phases present at two different ordering temperatures. A possible explanation for the second transition may be the high magnetic anisotropy and crystalline electric fields present in the sample. In order to determine the nature of the proposed magnetic phases, a resonant x-ray scattering experiment was performed and is discussed in this chapter. Though a modulated antiferromagnetic structure below 28 K was found, no evidence of a second magnetic phase was detected in the x-ray experiment down to a temperature of 6 K.

Sample Properties

The sample was grown in a similar high temperature solution growth technique as discussed for GdCo_2Ge_2 in the previous chapter. NdCo_2Ge_2 also has a tetragonal structure with the c-axis perpendicular to the platelet surface. The single crystal sample was characterized using a molybdenum K_α source. The mosaic of the grains within the multi-domain sample was measured to have a full width at half maximum of 0.016 degrees at the (0 0 8) charge reflection. The lattice parameters were found to be $a = b = 4.026 \text{ \AA}$ and $c = 10.1672 \text{ \AA}$ at $T = 6 \text{ K}$. This is consistent with previous measurements

for NdCo_2Ge_2 [13, 14].

The first step in determining the properties of NdCo_2Ge_2 was a SQUID susceptibility measurement. The results show two clear peaks with $T_N \approx 30$ K and another transition at $T_t \approx 10$ K in Fig. 5.1. This second peak suggests another magnetic phase as reported from neutron results[14]. In this neutron study, it is suggested that a commensurate AF structure appears at ~ 10 K. Evidence for the nature of this second phase could come from x-ray measurements of magnetic satellite peaks at $(0\ 0\ L)$ magnetic wave vectors where L is an odd integer. The search for these peaks is a principle aspect of this experiment. The absence of these peaks at the second transition temperature indicates there may be a different type of transition occurring. This will require further study in the future.

Figure 5.1 Susceptibility measurements with field $H = 1$ kOe applied parallel and perpendicular to the c -axis. Note the two peaks indicating two magnetic phases.

Magnetic X-ray Experiment

Due to the high wave vector resolution and elemental selectivity of the technique, an XRES experiment can play a vital role in determining the exact nature of the magnetic ordering in NdCo_2Ge_2 . To obtain the necessary intensity to study the magnetic peaks, the experiment was carried out at the Advanced Photon Source at Argonne National Laboratory. A double bounce, single crystal, Si-monochromator at the MUCAT (Sector 6-ID) beamline was tuned to the L_{II} resonant edge of Nd. This occurs at an incident photon energy of 6.722 KeV. Working at the resonance in Nd ensures that the detected magnetic scattering is from the moments on the Nd ions. These peaks are shown to be magnetic in Fig. 5.2 by measuring the same scattering vector below and above the transition temperature. It is generally found throughout the series that the moments reside exclusively on the rare-earth ion. This was tested by studying the sample at $E = 7.7$ KeV. This energy is close to the L_{III} edge for cobalt. Magnetic satellite peaks were not found at this energy indicating that the magnetic moment on the cobalt ion is small or zero.

Figure 5.2 Magnetic peak position (0 0 6.75) measured below and above the transition temperature.

By studying previous measurements and neutron data for the series, it was deter-

mined that the most likely position for the wave vector was along the c -axis. For this reason, a search was carried out for the modulation in the $(0\ 0\ L \pm \tau)$ direction. The magnetic peaks should be detectable below $T \approx 28$ K. The sample was cooled to 6 K using a closed cycle displax cryostat. The measurement was performed in a $\sigma \rightarrow \pi$ geometry that is sensitive to the resonant photons and suppresses charge and nonresonant scattering.

Results

A search along the $(0\ 0\ L)$ direction resulted in a resonant peak at $(0\ 0\ 6.741)$. This peak corresponds to an incommensurate antiferromagnetic structure with wave vector $(0\ 0\ \tau_z)$ and $\tau_z = 0.7420(\pm 0.0003)$ r.l.u. as shown in Fig. 5.3. This temperature dependent measurement shows the integrated intensity of the satellite peak $(0\ 0\ 8 - \tau_z)$ subtracted from the $(0\ 0\ 8)$ charge peak position. This value is consistent with the measurements using neutron diffraction for the incommensurate structure.

In a search for the predicted commensurate magnetic phase, no magnetic peaks were found. The commensurate structure predicts magnetic satellite peaks a distance of $\tau_z = 1.0$ r.l.u. away from the charge peaks present for the ThCr_2Si_2 -type structure [14]. Extensive measurements of the $(0\ 0\ 7)$, Fig. 5.4, and similar peaks failed to detect magnetic peaks. Translations of the sample to study different domains still did not result in magnetic peaks at positions $(0\ 0\ 7)$, $(0\ 0\ 5)$, $(1\ 0\ 6)$, and $(\frac{1}{2}\ 0\ 7)$.

In order to study the detected resonance at the $(0\ 0\ 6.741)$ position, energy scans were carried out at both the $(0\ 0\ 8)$ charge peak and the position of the magnetic peak. These are compared in Fig. 5.5. The position of the peak of the resonance above the maximum slope in the absorption curve is indicative of a dipole resonant process. This is important to the understanding of which energy levels are involved in the transitions.

For a precise determination of the transition temperature to the incommensurate

Figure 5.3 Temperature dependence of the wave vector in reciprocal space measured in relation to the (008) peak position using the (0 0 8- τ) satellite. The continuous change of the wave vector with temperature suggests that the ordering is incommensurate with the lattice.

state, a temperature dependent integrated intensity measurement was carried out as shown in Fig. 5.6. The detector was centered on the (0 0 6.741) magnetic peak and transverse θ scans were carried out. The detector slits were opened wide in order to ensure that all of the scattered photons were detected for the integrated intensity measurement. These peaks were then fit with a Lorentzian peak profile and the amplitude of each fit was used for the value of the integrated intensity. As the temperature is increased, the intensity of the peaks decreases until it disappears around the transition point of $28(\pm 0.2)$ K. A power law function was used to fit the data and determine an accurate value of the Néel temperature. The fit was $I = A(T_N - T)^{2\beta}$ where $T_N = 28$ K and $\beta = 0.26$.

In conclusion, NdCo_2Ge_2 orders antiferromagnetically at a transition temperature of $T_N = 28$ K with a magnetic wave vector of (0 0 0.742). After a careful search, no evidence of the reported commensurate structure was found down to a temperature of

Figure 5.4 Scans along the L direction in reciprocal space. (0 0 6.741) is shown in (a) and the (0 0 7) position is shown in (b). No peak was found in a search for the commensurate structure.

6K.

Figure 5.5 Energy scans through the Nd L_{II} edge. (a) The absorption at (0 0 8) charge peak. (b) The resonance of the (0 0 6.741) peak. Note the position of the resonant peak above the absorption edge.

Figure 5.6 Order parameter measurement of integrated intensity as the temperature is increased through the transition. The red line is a fit using $I = A(T_N - T)^{2\beta}$. Note that deviation from fit line occurs near temperature of second peak in susceptibility.

6 GENERAL CONCLUSIONS

The compounds GdCo_2Ge_2 and NdCo_2Ge_2 both exhibit antiferromagnetic ordering with the magnetic moments located on the rare-earth site. Careful study of the integrated intensity measurement gives an ordering wave vector along the c -direction of $(0\ 0\ \tau_z)$ where $\tau_z = 0.932(\pm 0.002)$ r.l.u. for GdCo_2Ge_2 with an ordering temperature of $32.9(\pm 0.2)$ K. For NdCo_2Ge_2 , $\tau_z = 0.7420(\pm 0.0003)$ r.l.u. below $T_N = 28(\pm 0.2)$ K. The moments were found to be in the basal plane for the gadolinium sample. No evidence for the reported second transition was found in the neodymium sample. The XRES technique plays an important role in determining these magnetic structures as demonstrated.

With an understanding of the ordering in the GdCo_2Ge_2 compound, it will be important to look at the magnetic ordering in other compounds in this series. Since the gadolinium compound has only minimal crystal electric field effects due to its half filled $4f$ shell, it will be possible to study the effect that the crystal electric field has on other members of the series by comparing the magnetic ordering in these compounds with the ordering for GdCo_2Ge_2 . An x-ray study of the EuCo_2Ge_2 compound could also clear up the question of whether a moment exists on the cobalt ion.

Finally, it will be important to carry out further experiments on the NdCo_2Ge_2 sample in order to determine the nature of the second magnetic phase below the Neel temperature that is suggested by susceptibility measurements.

It is through the careful comparison of experimental results with theoretical predictions that progress can be made in understanding the magnetic ordering of the RCo_2Ge_2

series. After performing measurements on each of the compounds, a more complete picture of the interactions involved in the magnetic ordering can be obtained.

BIBLIOGRAPHY

- [1] C. Song, *X-ray resonant exchange scattering investigations of rare earth intermetallic compounds: $TbNi_2B_2C$, $TbCu_2Ge_2$, and $GdAgSb_2$* . PhD dissertation, Iowa State University, 2001.
- [2] C. Song, W. Good, D. Wermeille, A. I. Goldman, S. L. Bud'ko, and P. C. Canfield, "Magnetic structure of $GdAgSb_2$ determined by x-ray resonant exchange scattering," *Phys. Rev. B*, vol. 65, no. 172415, 2002.
- [3] P. M. Platzman and N. Tzoar, "Magnetic scattering of x-rays from electrons in molecules and solids," *Phys. Rev. B*, vol. 2, p. 3556, 1970.
- [4] Doon Gibbs, D. R. Harshman, E. D. Isaacs, D. B. McWhan, D. Mills, and C. Vettier, "Polarization and resonance properties of magnetic x-ray scattering in holmium," *Phys. Rev. Lett.*, vol. 61, p. 1241, 1988.
- [5] M. Blume, "Magnetic scattering of x-rays," *J. Appl. Phys.*, vol. 57, no. 1, p. 3615, 1985.
- [6] Z. Islam, *The interplay of long-range magnetic order and single-ion anisotropy in rare earth nickel germanides*. PhD dissertation, Iowa State University, 1999.
- [7] M. Blume, "Magnetic effects in anomalous dispersion," *Reson. Anomalous X-ray Scattering*, pp. 495–512, 1994.

- [8] C. Detlefs, *X-ray resonant exchange scattering of rare-earth nickel borocarbide*. PhD dissertation, Iowa State University, 1997.
- [9] J. P. Hill and D. F. McMorrow, "X-ray resonant exchange scattering: Polarization dependence and correlation functions," *Acta Cryst.*, vol. 52, pp. 236–244, 1996.
- [10] C. Song, Z. Islam, L. Lottermoser, A. I. Goldman, P. C. Canfield, and C. Detlefs, "Magnetostriction-induced tetragonal-to-orthorhombic phase transition in $TbNi_2B_2C$," *Phys. Rev. B*, vol. 60, no. 9, 1999.
- [11] M. Blume and Doon Gibbs, "Polarization dependence of magnetic x-ray scattering," *Phys. Rev. B*, vol. 37, no. 4, 1988.
- [12] W. M. McCall, K. S. V. L. Narasimhan, and R. A. Butera, "Lattice parameters and powder diffraction data for 14 RCO_2Ge_2 compounds ($R = La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Y$)," *J. Appl. Cryst.*, vol. 6, p. 301, 1973.
- [13] W. M. McCall, K. S. V. L. Narasimhan, and R. A. Butera, "Magnetic properties of RCO_2Ge_2 compounds," *J. Appl. Phys.*, vol. 44, p. 4724, 1973.
- [14] G. André, F. Bourée-Vignerot, A. Oleś, and A. Szytula, "Magnetic structure of $NdCo_2Ge_2$ compound," *JMMM*, vol. 86, pp. 387–390, 1990.
- [15] Israel Felner and Israel Nowik, "Magnetism and hyperfine interactions in EuM_2Ge_2 and GdM_2Ge_2 ($M = Mn, Fe, Co, Ni, Cu$)," *J. Phys. Chem. Solids*, vol. 39, pp. 763–773, 1978.
- [16] M. Kolenda, A. Szytula, and A. Zygmunt, "Magnetic properties of RCO_2Si_2 and RCO_2Ge_2 compounds," *Cryst. Electr. Field Eff. f-Electron Magn., [Proc. Int. Conf.]*, vol. 4, pp. 309–17, 1982.

- [17] L. Vinokurova, V. Ivanov, and A. Szytula, "High-field magnetization in RCO_2X_2 compounds," *JMMM*, vol. 99, pp. 193–198, 1991.
- [18] J. Leciejewicz, A. Szytula, and A. Zygmunt, "Magnetic properties of $NdCo_2Ge_2$, $ErCo_2Ge_2$, and $PrCo_2Ge_2$ compounds," *Solid State Communications*, vol. 45, no. 2, pp. 149–152, 1983.
- [19] N. P. Duong, K. H. J. Buschow, E. Bruck, J. C. P. Klaasse, P. E. Brommer, L. T. Tai, and T. D. Hien, "Magnetic properties of GdT_2Ge_2 compounds ($T = 3d, 4d$)," *Journal of Alloys and Compounds*, vol. 298, pp. 18–25, 2000.
- [20] M. A. Ruderman and C. Kittel, "Indirect exchange coupling of nuclear magnetic moments by conduction electrons," *Phys. Rev.*, vol. 96, no. 1, 1954.
- [21] C. Kittel, "Indirect exchange interactions in metals," *Solid State Phys.*, vol. 22, no. 1, 1968.
- [22] T. Kasuya, "A theory of metallic ferro- and antiferromagnetism on Zener's model," *Prog. Theor. Phys.*, vol. 16, no. 45, 1956.
- [23] K. Yosida, "Magnetic properties of $Cu - Mn$ alloys," *Phys. Rev.*, vol. 106, no. 5, 1957.
- [24] F. M. Mulder, R. C. Thiel, and K. H. J. Buschow, " ^{155}Gd Mossbauer effect and magnetic properties of ternary rare earth compounds of the type RT_2Ge_2 ($T = 3d, 4d$)," *Journal of Alloys and Compounds*, vol. 202, pp. 29–35, 1993.
- [25] R. M. White, "Quantum theory of magnetism," *Springer Series in Solid State Sciences*, vol. 46, 1983.
- [26] P. C. Canfield and Z. Fisk, "Growth of single crystals from metallic fluxes," *Philos. Mag. B*, vol. 56, p. 7843, 1992.

- [27] Paul C. Canfield and Ian R. Fisher, "High temperature solution growth of inter-metallic single crystals and quasicrystals.," *J. Crystal Growth*, vol. 225, pp. 155–161, 2001.