Magnetic EXAFS at Gd L-edges: the spin-pair-distribution function of Gd neighbors

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The purpose of the experiment is to study the normal and the Magnetic EXAFS (MEXAFS) since EXAFS is the method of choice to investigate the local pair- and spin-pair-distribution function. We present MEXAFS and EXAFS measurements at the L-edges of a Gd single crystal in the temperature range of 10 K to 250 K. Therefore we are able to investigate the MEXAFS in a wide range of the reduced temperature $t=T/T_C$ of $0.04 \leq t \leq 0.85$ with T_C=293 K. We find a strong decrease of the nearest neighbor EXAFS which retains only about 35% of its 10 K value already at 250 K. This highlights the importance of lattice vibrations. To analyze the individual scattering contributions to the MEXAFS and the EXAFS, *ab initio* calculations (FEFF code) have been carried out. The comparison of the temperature-dependent damping of the normal EXAFS with the spin-dependent MEXAFS allows us to separate the influence of lattice vibrations (Debye temperature 160 K) from the magnetic ordering (Curie temperature) on the MEXAFS.

Keywords: temperature-dependent magnetic EXAFS

1. Introduction

Gd metal is a model system for the investigation of the magnetic EXAFS (MEXAFS) effect. The first MEXAFS oscillations were detected for a Gd metal foil at 100 K (Schütz *et al.*, 1989). Since then the Gd MEXAFS was discussed in various experimental (Dartyge *et al.*, 1995; Schütz & Ahlers, 1996; Ahlers & Schütz, 1998; Ahlers *et al.*, 1998) and theoretical works (Brouder *et al.*, 1995; Ankudinov & Rehr, 1995; Ebert *et al.*, 2000). Looking at the enormous work on this subject it is surprising that no temperature-dependent MEXAFS investigations of the L-edge MEXAFS were carried out yet, as it was already demonstrated for the 3*d* transition metals (Lemke *et al.*, 1998; Wende *et al.*, 1998; Wende *et al.*, 1999; Wende *et al.*, 2000). Nowadays the theoretical descriptions of the MEXAFS effect are quite advanced and describe the magnetism at T= 0 K including relativistic phenomena (Brouder *et al.*, 1996; Ankudinov & Rehr, 1997; Ebert *et al.*, 1999). Nevertheless, no prediction exists for the detailed temperature dependence of the MEXAFS which include, for instance, effects of spin-fluctuations on a nearest neighbor scale. Therefore, we carried out the first temperature-dependent study at the L-edges of a Gd single crystal. The relatively low Curie-temperature T_C of bulk Gd of 293 K allowed us to study the MEXAFS in a wide range of the reduced temperature $t = T/T_C$. The use of a single crystal sample enabled us to discuss high quality MEXAFS data with small static disorder at the L_3-edge up to k_{max}=13.0 Å^{-1}.

2. Experimental details

The *L*-edge MEXAFS data were recorded at the ID 12A beamline at the ESRF (Grenoble). For the detailed MEXAFS analysis the data at the L_3-edge were used because of the longer *k*-range compared to the L_2-edge range (which is limited by the L_1-edge). The Gd(0001) single crystal with a shape of a plate (c-axis normal to the surface) was mounted so that the x-rays were incident normal to the surface ($\vec{k}_{photon}||$c-axis). The data were recorded at 10 K, 100 K, 200 K and 250 K corresponding to reduced temperatures of t= 0.034, 0.34, 0.68 and 0.85. To ensure that the sample was completely saturated, the magnetization $M(H)$ versus the magnetic field was measured at each temperature point. Since the saturation field H_S was changing with temperature, the MEXAFS data were recorded at the same reduced field H/H_S=1.2. From the $M(H)$ curves the following applied magnetic fields for the MEXAFS measurements were determined: 3.0 T (10 K), 2.8 T (100 K), 2.5 T (200 K) and 2.0 T (250 K). The fluorescence of the sample was detected with silicon photodiodes (Gauthier *et al.*, 1995) and the resulting data were corrected for self-absorption effects (Tröger *et al.*, 1992). To measure the EXAFS and MEXAFS in the energy range of the 7185 eV to 8500 eV with a constant degree of circularly polarized x-rays the undulator gap-scan technique was used (Rogalev *et al.*, 1998). We measured the dichroic effect $\mu_M(E) = \mu^+(E) - \mu^-(E)$ for both possibilities i.e. changing the direction of the magnetization for a fixed helicity and changing the helicity of the x-rays for a fixed magnetization. Both methods revealed the same dichroic signal indicating that no experimental artifacts were observed. The EXAFS and MEXAFS oscillations were extracted with a standard spline-analysis as described in detail in (Wende, 1999). This means that for the investigation of the MEXAFS a smooth magnetic background was subtracted from the difference $\mu_M(E)$ in order to calculate the MEXAFS oscillations $\chi_M(k)$.

3. Results and discussion

The temperature-dependent EXAFS and MEXAFS data are presented in Fig. 1. The MEXAFS oscillations at the L_3-edge can be detected up to $k_{max} = 13$ Å^{-1}. The Fourier transformed data of the EXAFS and the MEXAFS exhibit a clear splitting of the main peak due to the so-called Ramsauer-Townsend (RT) resonance. The splitting of the main peak corresponds to a minimum of the enveloping amplitude in *k*-space at about $k = 9$ Å^{-1}. This indicates a clear improvement of the quality of the MEXAFS data compared to spectra published previously where these features could not be detected (Dartyge *et al.*, 1995; Ahlers & Schütz, 1998). One reason might be that the measurements in earlier works were not carried out with a single crystal but with metal foils at 100 K (Schütz *et al.*, 1989). Therefore one expects a much stronger effect of static and dynamic disorder on the EXAFS and the MEXAFS compared to the results for a Gd single crystal at 10 K as presented here. Furthermore, a *k*-weighting of k^1 was used in our work, whereas the Fourier transforms of the simple EXAFS ($|FT[\chi(k)]|$) and MEXAFS ($|FT[\chi_M(k)]|$) oscillations are discussed in the earlier works (Schütz *et al.*, 1989, Schütz & Ahlers, 1996; Ahlers & Schütz, 1998). As shown in Fig. 1 a clear temperature dependence for the EXAFS as well as the MEXAFS can be determined. For a quantitative analysis of the reduction of the Fourier transform (FT) intensities we carried out a fit of the main peak in *R*-space using the FEFFIT code. The fit shows that the reduction of the intensity of the main peak can be accurately described by means of the correlated

Debye model. This indicates that the FT intensities of the EXAFS can be used in a first approximation as a measure of the influence of Debye-Waller factor $e^{-2\sigma^2k^2}$ on the spectra. This is of importance for the comparison of the temperature dependence of the MEXAFS with the EXAFS as discussed later. With the FEFFIT analysis of the EXAFS data a Debye temperature of $\theta_D = (160 \pm 7)$ K is calculated in good agreement with 163.4 K given in the literature from heat capacity measurements (Tsang *et al.*, 1985). This value is relatively low compared for instance to 3*d* transition metals, where values of about θ_D=350-450 K are found. Assuming that this value also holds for a Gd metal foil, the strong damping already at T=100 K (where the earlier MEXAFS works have been carried out (Ahlers & Schütz, 1998)) can be explained. In our experiment we find that at T=250 K the thermal disorder leads to a damping of the height of the main peak in the EXAFS Fourier transform of 35% of the T=10 K value (see Fig. 1). A similar damping is found for the MEXAFS: Starting with the analysis in *k*-space a damping of the exponential form $e^{-2\sigma^2k^2}$ can be determined. Although the MEXAFS wiggles $\chi_M(k)$ at k=4.5 Å^{-1} are damped at T=250 K to about 50% of their T=10 K value, they are hardly detectable for k=10.0 Å^{-1} at T=250 K whereas obvious wiggles can be seen at T=10 K for the higher *k*-range. This indicates that the thermal disorder also influences the magnetic EXAFS signal. As already discussed the effects of static and dynamic disorder can be minimized by using a single crystal at 10 K. The effect of this minimization is obvious in the Fourier transform of the MEXAFS oscillations at 10 K where a similar splitting of the main peak can be determined for the MEXAFS as it was seen for the EXAFS.

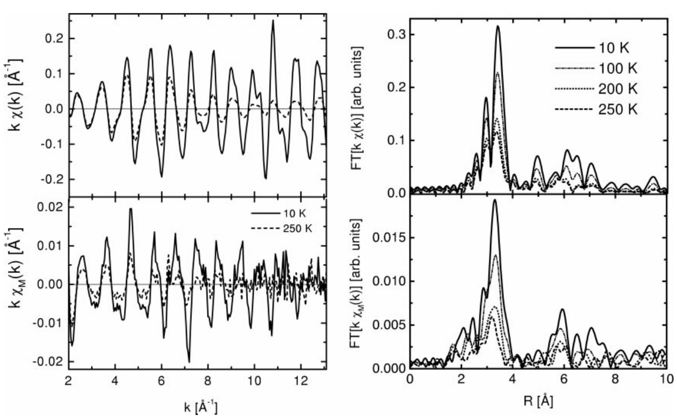

Figure 1
Temperature-dependent L_3-edge EXAFS (top) and MEXAFS (bottom) oscillations (left) $k \cdot \chi(k)$ and $k \cdot \chi_M(k)$, and the corresponding Fourier transforms (right) $|FT[k \cdot \chi(k)]|$ and $|FT[k \cdot \chi_M(k)]|$. An obvious temperature-dependent damping can be seen for both cases. For the EXAFS and the MEXAFS Fourier transforms a clear splitting of the main peak due to the so-called Ramsauer-Townsend resonance can be detected.

Before discussing the effect of temperature dependence of the magnetization $M(T)$ on the MEXAFS intensity we first turn to the comparison of the experimental data at 10 K to *ab initio* calculations carried out with the FEFF7 code using Gd bulk structure. The results are presented in Fig. 2. The agreement of the experimental EXAFS with the calculation is perfect in *k*-space as well as in *R*-space: All the fine structures seen e.g. at k=10.0 Å^{-1} and k=11.5 Å^{-1} are reproduced in the calculation. Also the enveloping amplitude in *k*-space in the calculation agrees very well with the experimental data. This can also be seen in *R*-space, where the splitting of the main peak (RT resonance) as well as the intensities and positions of the peaks at larger distances are correctly described. The presented calculations are carried out including single-scattering and multiple-scattering effects. If one calculates the EXAFS without multiple-scattering contributions one finds higher intensities of the peaks at about R=6 Å (not shown). This shows that in the case of Gd the multiple-scattering contributions interfere destructively with the single-scattering contributions of larger scattering shells. This effect is correctly reproduced by the FEFF code. The agreement of the experimental MEXAFS data with the calculation is also fairly good. The phase shift of about $\pi/2$ of the MEXAFS oscillations $\chi_M(k)$ compared to the EXAFS oscillations $\chi(k)$ is correctly described. The enveloping amplitude of the calculation is in reasonable agreement with the experimental data. Therefore the splitting of the main peak in the MEXAFS Fourier transform is reproduced in the calculation. Deviations between theory and experiment can be detected in the Fourier transform at larger distances in the range of 4.0 Å to 8.0 Å. These differences are not due to the feature seen at k=6.3 Å^{-1} which can be assigned to the so-called magnetic multi-electron excitations (MMEEs) (Schütz & Ahlers, 1996; Ahlers & Schütz, 1998). More serious are the differences seen in the *k*-space in the range of k=7.0 Å^{-1} to k=8.5 Å^{-1}. As the negative and the positive part of the experimental wiggle is larger compared to the calculated data, it is not very likely that this difference is also due to multi-electron excitations as these lead to an additional feature only. Therefore, we assign the main differences to scattering effects. It was already discussed for the normal EXAFS data that the single-scattering contributions interfere destructively with the multiple-scattering contributions. One possible explanation for the differences between the experimental MEXAFS data and the calculation could be that the phase of the multiple-scattering contributions which have been found to be enhanced for the MEXAFS case (Wende *et al.*, 1999) are not described accurately enough in the calculation. This question will be the focus of a forthcoming publication because the main task of the present work is the analysis of the temperature dependence of the EXAFS and the MEXAFS.

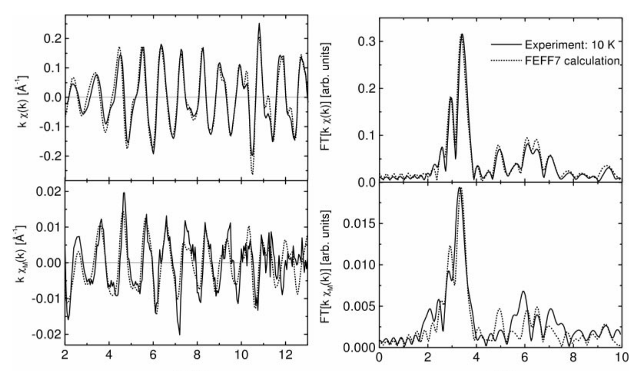

Figure 2
Comparison of the experimental EXAFS (top) and MEXAFS (bottom) data at 10 K to *ab initio* calculations (FEFF7). The calculations show good agreement for the enveloping amplitude and phase in *k*-space as well as in *R*-space for the splitting of the main peak (RT resonance) and the peaks at larger distances.

Here we want to investigate the temperature dependence of the main peak only. As this peak is splitted due to the RT resonance the integrated signal of the main peak in the EXAFS and MEXAFS Fourier transforms in the range of R=2.0-4.0 Å will be discussed. In Fig. 3 we compare the experimental results to the temperature dependence of the magnetization under applied magnetic fields as given in the literature (Nigh *et al.*, 1963). In order to do so we scaled all the experimental data (the near-edge MCXD intensity, the integrated EXAFS and MEXAFS main peaks) to match the literature at the lowest temperature (10 K). This means that relative changes are compared. As expected the temperature dependence of the MCXD signal follows the temperature dependence of the magnetization $M(T)$. In the present investigation we were able to probe the MEXAFS up to 250 K which corresponds to a reduced temperature of $t = 0.85$. At this temperature the magnetization is damped to 58% of its 10 K value. This was not possible in earlier temperature-dependent MEXAFS investigations on 3*d* transition metals, where a reduced temperature of $t = 0.38$ only was reached (Wende *et al*, 1998; Wende *et al.*, 1999). As shown in Fig. 3 the MEXAFS signal is reduced at T=250 K to 31% of its 10 K value. This indicates that the lattice vibrations and the reduction of the magnetization influence the temperature dependence of the MEXAFS. This damping must be compared to the reduction of the normal EXAFS signal which is due to lattice vibrations only. For the EXAFS case a reduction at T=250 K to 46% of its 10 K value is determined. Assuming that the temperature dependence of the magnetization $M(T)$ and the EXAFS Debye-Waller factor $e^{-2\sigma^2 k^2}$ describe the MEXAFS in a multiplicative way, the experimental MCXD signal has to be scaled with the EXAFS signal leading to reduction at 250 K of *Intensity(MCXD)·Intensity(EXAFS)*=0.58·0.46=0.27 which has to be compared to the MEXAFS intensity of (0.31±0.04). This simple calculation indicates that the assumption that the magnetization and the EXAFS Debye-Waller factor have to be multiplied to describe the temperature dependence of the MEXAFS is correct for the Gd case. Further theoretical work is needed to interpret these experimental findings which differ from the results obtained for 3*d* transition metals. (Wende *et al.*, 1998; Wende *et al.*, 1999). One reason for this difference could be the more localized nature for the 4f rare-earth metals compared to the itinerant character of the 3*d* transition metals.

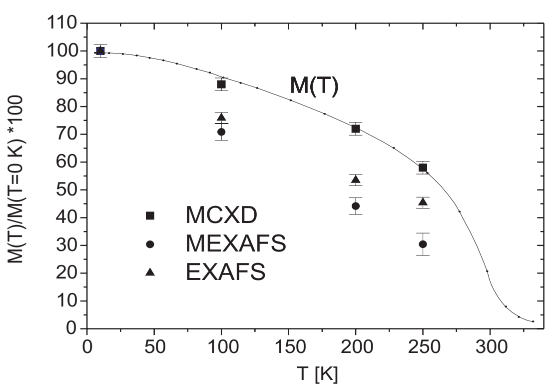

Figure 3
Reduced magnetization M(T)/M(T=0 K) as a function of temperature. The solid line is taken from literature (Nigh *et al.*, 1963). The experimental data are calculated from the L_3-edge near-edge MCXD intensity (squares), from the integrated main peak of the EXAFS (triangles) and the MEXAFS (circles) Fourier transforms. The MCXD, EXAFS and MEXAFS data are scaled to match the literature at the lowest temperature (10 K).

4. Conclusion

We carried out the first temperature dependent MEXAFS investigation at the Gd *L*-edges. The use of a Gd single crystal at low temperatures enabled us to minimize effects of the static and dynamic disorder. Therefore we are able to identify the influence of the Ramsauer-Townsend resonance on the EXAFS and the MEXAFS. *Ab initio* calculations carried out with the FEFF code are in good agreement with the experimental EXAFS and MEXAFS data. By means of these calculations it was found that the multiple-scattering contributions interfere destructively with the single-scattering contributions. The measurements in the temperature range of 10 K to 250 K allowed for an analysis of the near-edge MCXD, the EXAFS and the MEXAFS signals in a wide range of the reduced temperature ($0.04 \le t \le 0.85$). The present work shows that MEXAFS is the technique of choice to measure spin- and site-selective pair-distribution functions.

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