Magnetic EXAFS calculations for disordered alloys

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A fully relativistic scheme is presented that allows one to describe the magnetic Extended X-ray Absorption Fine Structure (MEXAFS) in disordered systems. This method is based on a combination of the relativistic multiple scattering theory and the Coherent Potential Approximation (CPA) alloy theory. The alloy systems Fe_xCo_{1-x} and Fe_xPt_{1-x} are used to illustrate the ability of this theoretical approach due to the availability of suitable experimental data. For the latter system a rather pronounced impact of the degree of order on the MEXAFS has been found.

Keywords: disordered systems; multiple scattering theory; EXAFS; magnetic dichroism.

1. Introduction

Substitutional randomly disordered alloys are a very important and interesting class of materials because the concentration – seen as a free parameter – allows one to vary their physical properties within a certain range in a continuous manner. Several theoretical models, which aim to provide an adequate description of the electronic structure of such alloys, have been developed during the last 50 years. Among these the Coherent Potential Approximation (CPA) alloy theory suggested by Soven(Soven, 1967) has emerged to play a prominent role as it is able to provide a highly reliable description of a wide range of materials at relatively low numerical costs. Indeed, the CPA has proved to be the best possible among the so-called single site alloy theories that assume complete random disorder and ignore short-range order (Faulkner, 1982). Combining the CPA with multiple scattering theory or the Korringa-Kohn-Rostoker (KKR) method of band structure calculation leads to a computational scheme (KKR-CPA) which is applied nowadays routinely for quantitative investigations of the electronic properties of disordered alloys (Faulkner, 1982; Stocks & Winter, 1984).

X-ray absorption is a local process and so the corresponding absorption coefficient may be derived in terms of the underlying electronic structure, for the case of random alloys using a KKR-CPA approach, within the framework of multiple scattering theory. This also applies in same way to the X-ray emission process which is complementary to X-ray absorption. In fact, the KKR-CPA was first applied to deal with X-ray emission of disordered alloys. The corresponding expression for the X-ray emission intensity, which is essentially identical to that of the related absorption coefficient, was derived by Durham et al. (Durham et al., 1979) in a non-relativistic and by Staunton et al. (Staunton et al., 1980) in a fully relativistic way. However, these schemes did not allow one to deal with magnetic dichroism because they neglected relativistic effects and/or spin-magnetism. The first investigations of the magnetic X-ray dichroism (MXD) in alloys were performed by Ebert et

al. (Ebert, 1993; Ebert et al., 1993) who developed an appropriate fully relativistic scheme based on the KKR-CPA. This formalism, which treats all possible sources of the MXD on an equal footing, is extended here to get access to the EXAFS region as well. A short description of the basic formalism is given in the following and some illustrative results are presented.

2. Theoretical framework

The starting point for our formalism is the expression for the X-ray absorption coefficient $\mu^{\vec{q}\lambda}(\omega)$:

$$\mu^{\vec{q}\lambda}(\omega) \quad \propto \quad \sum_{i\,occ} \left[\sum_{\Lambda\Lambda'} M_{\Lambda i}^{\vec{q}\lambda*}(E_f)\tau_{\Lambda\Lambda'}^{nn}(E_f)M_{\Lambda' i}^{\vec{q}\lambda}(E_f) \right.$$

$$\left. + \sum_{\Lambda} I_{\Lambda i}^{\vec{q}\lambda}(E_f) \right] \tag{1}$$

which can be derived within the framework of relativistic multiple scattering theory for magnetic solids (Ebert, 1996). Here $M_{\Lambda i}^{\vec{q}\lambda}$ are the appropriate matrix elements with i denoting the core states involved in the absorption process. The relativistic spin-orbit and magnetic quantum numbers, κ and μ, respectively $(\Lambda = (\kappa, \mu))$ specify the partial waves that describe the final states at energy E_f. The additional superscripts $\vec{q}$ and λ represent the wave vector and polarization of the radiation with frequency ω. The quantity $\tau_{\Lambda\Lambda'}^{nn'}$ is the so-called scattering path operator which transfers a wave with spin-angular character Λ' incoming at site n' into a wave with character Λ outgoing from site n taking all possible multiple scattering events into account. Finally, the last term $I_{\Lambda i}^{\vec{q}\lambda}$ is a pure atomic-like contribution that occurs only if one works at complex energies (Ebert, 1996).

As only the site-diagonal scattering path operator $\tau_{\Lambda\Lambda'}^{nn}$ is used in Eq. (1), it is relatively straightforward to extend this expression so that it may be applied to disordered alloys. The corresponding absorption coefficient $\mu_{\alpha}^{\vec{q}\lambda}$ for an alloy-component α is obtained by evaluating the component-specific matrix elements $M_{\Lambda i}^{\vec{q}\lambda,\alpha}$ and inserting the component-projected scattering path operator $\tau_{\Lambda\Lambda'}^{nn,\alpha}$.

Within the CPA alloy theory the configurationally averaged properties of a disordered alloy are represented by a hypothetical ordered CPA-medium, which in turn may be described by a corresponding scattering path operator $\tau_{\Lambda\Lambda'}^{nn,CPA}$. This operator is determined by the CPA-condition:

$$x_A \underline{\tau}^{nn,A} + x_B \underline{\tau}^{nn,B} = \underline{\tau}^{nn,CPA} \quad , \tag{2}$$

where the matrices are defined with respect to the index Λ and the binary alloy system has components A and B at relative concentrations x_A and x_B, respectively. The above equation represents the requirement that the concentration-weighted sum of the component-projected scattering path operators $\underline{\tau}^{nn,\alpha}$ should be identical to that of the CPA-medium; i.e. embedding an A- or a B-atom into the CPA-medium should not cause any additional scattering.

The $\underline{\tau}^{nn,\alpha}$ describes the scattering properties of an α-atom embedded in the CPA-medium, i.e. of a substitutional impurity and is given by the expression

$$\underline{\tau}^{nn,\alpha} = \underline{\tau}^{nn,CPA} \left[1 + \left(\underline{t}_\alpha^{-1} - \underline{t}_{CPA}^{-1} \right) \underline{\tau}^{nn,CPA} \right]^{-1} \tag{3}$$

where $\underline{t}_\alpha$ and $\underline{t}_{CPA}$ are the single site t-matrices of the component α and of the CPA-medium, respectively. The later quantity is connected with the CPA scattering path operator by the relation

$$\underline{\tau}^{CPA} = \left(\underline{t}_{CPA}^{-1} - \underline{G} \right)^{-1} \quad , \tag{4}$$

where $\underline{G}$ is the real space structure constants matrix and the double lines indicate that all quantities are now matrices with respect to the spin-angular index Λ as well as the sites n. Accordingly, the dimension of these matrices is infinite for an infinite solid.

To obtain the quantities $\underline{t}_{CPA}$ and $\underline{\tau}^{nn,CPA}$, for given concentrations x_α, one must solve Eqs. (2)-(4) iteratively. For spatially ordered systems and relatively low energies – which usually includes the XANES region – Eq. (4) is replaced by the expression

$$\underline{\tau}^{nn,CPA} = \frac{1}{\Omega_{BZ}} \int_{\Omega_{BZ}} d^3k \left[\underline{t}_{CPA}^{-1} - \underline{G}(\vec{k}, E) \right]^{-1} \quad (5)$$

and, as a consequence, all multiple scattering events for the final states are included for the ordered CPA-medium. This approach has been applied with great success in the past to deal with the magnetic dichroism in the XANES region.

However, one cannot use this expression for the EXAFS-region due to numerical problems. Instead of this, multiple scattering is dealt with only for a finite cluster of atoms making use of the real space KKR equation (4). Altogether, this means that the CPA-equations (2)-(4) are solved in a first step for a finite cluster of atoms to yield $\underline{t}_{CPA}$ and $\underline{\tau}^{nn,CPA}$. In the following step, the absorption coefficient $\mu_\alpha^{q\lambda}$ for component α is calculated using Eq. (1) with the component-projected scattering path operator $\underline{\tau}^{nn,\alpha}$ obtained from Eq. (3). The matrix elements $M_{\Lambda i}^{q\lambda}$ are not affected by the CPA-procedure, i.e. they are evaluated in the usual way (Ebert, 1996). This also applies to the additional contributions $I_{\Lambda i}^{q\lambda}$ because these are component-specific and atomic-like; i.e. they are not connected to the multiple scattering problem dealt with within the CPA framework.

3. Results and discussion

In the following, results obtained by application of the above scheme to the alloy systems bcc-Fe_xCo_{1-x} and fcc-Fe_xPt_{1-x} will be presented. As a first step in both cases, the corresponding ground state potentials were determined self-consistently. For the calculation of the EXAFS- and MEXAFS-spectra, no self-energy corrections have been added but corresponding broadening corrections have been applied only afterwards (Ebert, 1996). The Debye-Waller thermal broadening factor has also been ignored for all calculations presented below.

3.1. The alloy system bcc-Fe_xCo_{1-x}

First experimentally investigations of MXD at the K-edge of Fe and Co in bcc-Fe_xCo_{1-x} were done by Stähler et al. (Stähler et al., 1993) for energies within the XANES region. Similar work was done by Pizzini et al. (Pizzini et al., 1994) who extended the range of the final state energy up to about 240 eV above the absorption edge. These authors found the Fe- and Co-spectra to be very similar with a rather weak dependence on the concentration.

The system Fe-Co forms over a wide range of concentrations ($0 \le x_{Fe} \le 0.8$) disordered substitutional alloys having bcc-structure. It is anticipated that, for these systems, no pronounced short-range order effects occur and so the CPA should be a suitable approach for a theoretical study of this alloy system. Corresponding results for the K-edges of Fe and Co have been presented in the past for the XANES-region (Ebert, 1993; Ebert et al., 1993). Application of the scheme described above allowed one to extend the energy range so that it covered the whole of the EXAFS-region. The resulting EXAFS- and MEXAFS-spectra of Fe and Co were found – in agreement with the above mentioned experimental work – to be very similar to that of pure bcc-Fe (Ebert et al., 1998b). It is only

in the near-edge region that noteworthy differences occur. Moreover for both components, in agreement with experiment, there is only an extremely weak variation of the EXAFS- and MEXAFS-spectra with concentration.
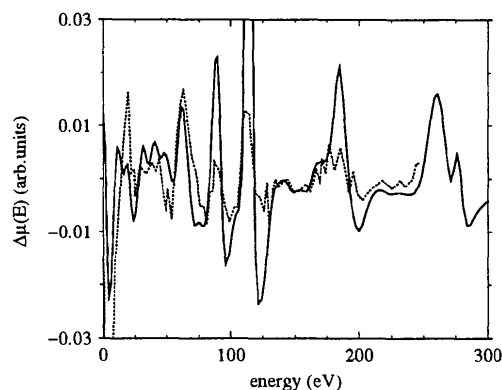
Figure 1

Magnetic EXAFS at the K-edge of Fe in the disordered alloy system bcc-$Fe_{0.7}Co_{0.3}$. Calculations (full line), compared against the experimental data (dotted line) (Pizzini et al., 1994).

The results for the MEXAFS-spectra of Fe in bcc-$Fe_{0.7}Co_{0.3}$ are shown in Fig. 1, where $\Delta\mu_K = \mu_K^+ - \mu_K^-$ is defined as the difference in absorption for left and right circularly polarized radiation. It is evident that the MXD signal is of the same order of magnitude throughout the range of energy presented. However, as the self-energy corrections and the Debye-Waller factor have not been included within the calculations, the oscillations in the (M)EXAFS-spectra are scarcely damped at high energies as observed in the corresponding experimental spectra (see Fig. 1).

Despite this, the agreement of our theoretical EXAFS- and MEXAFS spectra with available experimental data is quite satisfactory and one may conclude that the calculation of the (M)EXAFS-spectra for bcc-Fe_xCo_{1-x}, using the CPA alloy theory, gives an appropriate description of this disordered alloy system.

3.2. The alloy system Fe_xPt_{1-x}

The system Fe_xPt_{1-x}, like bcc-Fe_xCo_{1-x}, has been extensively investigated in recent years. Of particular note is the study of MXD at the $L_{2,3}$-edges of Pt in the XANES-region for the disordered alloys by Mayurama et al. (Maruyama et al., 1992). Corresponding theoretical studies, by Ebert et al. (Ebert et al., 1993), have supplied a detailed and quantitative description of this spectra. One of the most prominent features of the alloy system fcc-Fe_xPt_{1-x} is that it exhibits invar behaviour for $x_{Fe} \simeq 0.72$ in both the ordered and disordered state. This has lead to the extensive study of the properties of this material in its invar state.

Experimental data for the L_3-edge of Pt in ordered Fe_3Pt are shown in Figs. 2 and 3. The sample used for these measurements was somewhat off-stoichiometric ($x_{Fe} = 0.72$). Nevertheless, using X-ray diffraction it was found to be reasonably ordered and of Cu_3Au-structure. Consequently, initial calculations of the X-ray absorption spectra were done for a perfectly ordered Fe_3Pt system and the corresponding spectra are shown in Figs. 2 and 3 (full lines). Comparison of these spectra with the corresponding experimental spectra indicates that there is a fairly good agreement for both the conventional (Fig. 2) as well as the dichroic (Fig. 3) spectrum. However, due to the technical reasons given above, the peaks
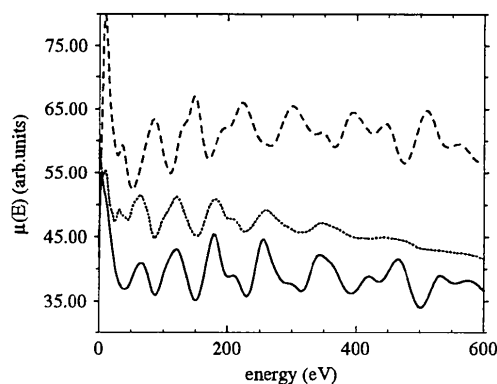
Figure 2
EXAFS at the L_3-edge of Pt in Fe_3Pt. Calculations for the ordered compound (full line), for the disordered system $Fe_{0.72}Pt_{0.28}$ (dashed line) compared against the experimental data (dotted line) (Ahlers, 1998). The spectra are shifted along the vertical axis.

of the theoretical spectra are more pronounced than their experimental counterparts.

To investigate the consequences of disorder additional calculations have been done using the CPA scheme for the disordered alloy $Fe_{0.72}Pt_{0.28}$. The resulting spectra have been added to Figs. 2 and 3 (dashed lines). As one notes, the theoretical curves strongly deviate from the experiment around the peak positions for the conventional (Fig. 2) as well as the dichroic (Fig. 3) spectrum.

In Fig. 3, showing the dichroic MEXAFS-spectra, one sees an appreciable dichroic signal throughout the whole investigated energy range. A simple interpretation of the energy dependence of this dichroic signal may be given in terms of the spin- and orbital polarisation using the sum rules as it is discussed elsewhere (Ebert *et al.*, 1998a; Ebert *et al.*, 1998b). This interpretation implies that the manifestation of a dichroic signal is an unambiguous indication of the occurrence of a magnetic moment on the Pt-sites which has been induced by the alloy partner Fe. The fact that the dichroic curves for ordered Fe_3Pt and disordered $Fe_{0.72}Pt_{0.28}$ in Fig. 3 have amplitudes in the same order of magnitude indicates that the average Pt magnetic moment in both systems should be quite similar. This is in full accordance with the theoretical moments deduced directly from the band structure calculations.

4. Summary

A scheme has been presented that allows a fully relativistic calculation of EXAFS-spectra for disordered alloys on the basis of the CPA alloy theory. This approach, which is suitable for both paramagnetic and ferromagnetic alloy systems, has been used to describe the ferromagnetic alloys $bcc\text{-}Fe_xCo_{1-x}$ and $fcc\text{-}Fe_xPt_{1-x}$. In particular, MEXAFS, i.e. magnetic dichroic spectra, have been presented and discussed together with corresponding theoretical conventional EXAFS-spectra as well as available experimental data.
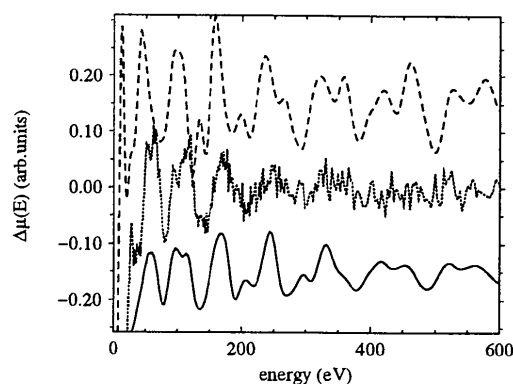
Figure 3
Magnetic EXAFS at the L_3-edge of Pt in Fe_3Pt. Calculations for the ordered compound (full line), for the disordered system $Fe_{0.72}Pt_{0.28}$ (dashed line) compared against the experimental data (dotted line) (Ahlers, 1998). The spectra are shifted along the vertical axis.

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