Magnetic circular dichroism in X-ray fluorescence of Heusler alloys at threshold excitation


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Received 7 April 2000; accepted 6 October 2000 by P. Dederichs

Abstract

The results of fluorescence measurements of magnetic circular dichroism (MCD) in Mn L_{2,3} X-ray emission and absorption for Heusler alloys NiMnSb and Co_{2}MnSb are presented. Very intense resonance Mn L_{3} emission is found at the Mn 2p_{3/2} threshold and attributed to a peculiarity of the threshold excitation in materials with a half-metallic character of the electronic structure. The excitation energy dependence of Mn L_{2,3} X-ray emission spectra (XES) was measured at beamline ID12B at the European Synchrotron Radiation Facility (ESRF, Grenoble) using 83% circularly polarized X-rays. A very large MCD effect found in XES is attributed to strong exchange splitting of spin-up and spin-down Mn 3d states. The anomalously high ratio of L_{2} emission intensity to L_{3} emission intensity is found.

Keywords: A. Magnetically ordered materials; D. Electronic states (localized); D. Recombination and trapping; E. Synchrotron radiation; E. X-ray emission

PACS: 75.20.Hr; 78.70.En; 75.25.+z; 73.90.+f

1. Introduction

First-principles spin-polarized calculations showed that the electronic structure of Heusler alloys has a metallic character for majority-spin electrons but an insulating character for minority-spin electrons. This can induce a half-metallic ferromagnetic state and a band gap near the Fermi level [1–3]. Magnetic circular dichroism (MCD) in X-ray emission spectra (XES) is predicted theoretically in Ref. [4], based on the fully relativistic spin-polarized band structure calculations for iron. Experimentally, this effect was confirmed for pure Fe in Ref. [5] and then used for the study of electronic structure of other magnetic systems such as Fe, Co and Ni [6], Rh, Rh_{2}Fe_{75} and Ni_{40}Fe_{55} [7], and Fe–Co alloys [8]. In this article we present the results of the magnetic dichroism measurements in Mn 2p X-ray emission and absorption for Heusler alloys NiMnSb and Co_{2}MnSb using an energy-selective monochromatic excitation with circularly polarized X-rays. The combination of the circular polarized X-ray light and external magnetic field is a very powerful technique that was applied, to our knowledge, for the first time for the investigation of magnetic dichroism in half-metallic alloys.

2. Experiment

The MCD XES measurements were performed on the beamline ID12B at the European Synchrotron Radiation Facility (ESRF). This beamline consists of a Dragon-like spherical grating monochromator producing about 83% circularly polarized X-rays. The extraordinarily low emittance of the 6 GeV stored electron beam allowed us to refocus the X-ray beam that passes the monochromator exit slit into a spot with dimensions of about 40 μm X 0.8 μm.
mm without excessive loss of intensity. The permanent magnet (NdFeB) devices were used to magnetize the sample for a fixed magnetization direction with $H = 2\ \text{T}$. The angle between incidence photons direction and sample surface was about $5^\circ$. The X-ray emission spectrometer consisted of an entrance 20 $\mu$m slit, three spherical diffraction gratings and a two-dimensional position-sensitive multi-channel detector [9]. It was oriented with its optical axis perpendicular to the incident X-rays, in a vertical dispersive geometry, and was operated with a 1200 lines/mm grating in second order of diffraction at a spectral resolution of 0.7 eV. A single crystal of NiMnSb and a polycrystalline sample of Co$_2$MnSb were taken for X-ray fluorescence measurements in vacuum $10^{-8}$–$10^{-9}$ Torr. The samples were scraped in vacuum of $10^{-6}$ Torr before the measurements.

3. Results

The Mn 2p X-ray absorption spectrum (XAS) excited in a total electron yield (TEY) mode shows dichroism of different signs (Fig. 1a) at the L$_3$ and L$_2$ thresholds. Mn 2p XES measured at the L$_3$ threshold ($E_{\text{exc}} = 640.5$ eV), at the L$_2$ threshold ($E_{\text{exc}} = 652$ eV) and far above threshold ($E_{\text{exc}} = 680$ eV) excitation show quite different fine structures. The Mn L$_3$ XES (2p$_{3/2} \rightarrow 3d4s$ transition), obtained at $E_{\text{exc}} = 640.5$ eV (Fig. 1b), has two subbands A and B located at 637.0 and 640.5 eV, respectively. The B peak shows dichroism with the same sign as was found for a Mn L$_3$ XAS, and the energy position of peak B (Fig. 1b) corresponds to the energy of L$_3$ absorption edge (Fig. 1a). In Fig. 1b the subband B is an elastic peak with photon energy corresponding to the excitation energy 640.5 eV. The intensity of elastic peak is usually rather weak for pure metals and alloys [6,10,11]. However in the present case, the intensity of the elastic peak B is found to be about 1.5 times higher than that of the normal emission peak A for resonant Mn L$_3$ XES.

In the Mn 2p XES (Fig. 1c) excited at the L$_2$ threshold excitation ($E_{\text{exc}} = 652$ eV), we found large changes in the intensity distribution. Peak A is merged with peak B forming a rather wide L$_3$ emission band. The main intensity A’ is due to the Mn L$_2$ X-ray emission transition (2p$_{1/2} \rightarrow 3d4s$). The L$_2$ XES again shows two peaks A’ and B’ located at emission energies of 648.2 and 652.0 eV (with Fermi level in between these peaks) corresponding to the normal emission (peak A’) and elastic scattering (peak B’), respectively. The intensity ratio $I(\text{B’})/I(\text{A’})$ in Mn L$_2$ XES is found to be opposite with respect to $I(\text{B})/I(\text{A})$ of the Mn L$_3$ XES in Fig. 1b. The relative dichroism value of the Mn L$_2$ XES (peak A’, Fig. 1c) measured at the L$_2$ threshold is found to be higher than that of the Mn L$_3$ XES (peak A, Fig. 1b) measured at the L$_3$ threshold whereas no dichroism of the Mn L$_2$ (peak B’, Fig. 1c) was found comparing to Mn L$_3$ (peak B, Fig. 1b). The sign of MCD in the Mn L$_2$ XES is opposite to that in the Mn L$_3$ XES.

Fig. 2 shows MCD in Mn X-ray emission for polycrystalline Co$_2$MnSb excited by right- and left-polarized radiation at $E_{\text{exc}} = 640.5, 644, 652$ and 680 eV. As is seen, the XES MCD behaviour for Co$_2$MnSb is found to be almost the same as that for NiMnSb.
not only due to the core-hole lifetime broadening, but also because of lifetime of intermediate (core-excited) state. Although the depolarization of X-ray emission photons may take place and weaken the dichroic effect, due to experimental conditions, the remaining part of intensity comes from polarized core-hole and reflects the spin-dependent DOS. The Fermi energy determined from the Mn 2p_{3/2} core level photoemission spectra of Heusler alloys [14,15] is resided at the intensity minimum of Mn L_3 between two subbands A and B. It means that the B subband corresponds to the X-ray emission from previously unoccupied 3d states, which are strongly populated during near-threshold excitation of the Mn 2p_{3/2} electron into the conduction band (Figs. 1a, 2a and b). Peak B arises due to photo-excited electron relaxation into the long lifetime states (a spin-down trap) above 1.5 eV up to the Fermi energy and further fluorescence transition to 2p level, with a spin conservation. This process was indicated as re-emission. In Heusler alloys under investigation, the relative intensity /I(B)//I(A) is anomalously high (Figs. 1b, 2a and b) for corresponding excitation energies near the L_3 threshold. Let us consider XES in Fig. 2b obtained at intermediate excitation energy E_{exc} = 644 eV specifically. The elastic peak C shows no dichroism, because of excitation to a non-polarized spin state. At L_3 XES one can see a two-band structure, consisting of A and B peaks, where the peak B shows negative dichroism sign. The intense additional contribution B at the L_3 XES is due to high re-emission. In cases of L_3 threshold excitation (Figs. 1b and 2a), the intensity of the B peak is defined by the sum of elastic scattering contribution and re-emission contribution. Re-emission contribution brings dichroism with maximum at 640.5 eV that corresponds to the energy of the Mn L_3 absorption edge, which explains both high intensity of elastic peak B at L_3 threshold excitation and non-zero dichroism at the L_3 emission, above the 2p_{3/2} core-level binding energy.

The dichroism helps to understand the process of re-emission. The elastic peak B has dichroism of negative sign as that observed near the L_3 threshold excitation (peak A) (Figs. 1b, 2a and b), that is, opposite to dichroism sign of the L_3 emission A' at the L_2 threshold excitation (Figs. 1c and 2c). We note that in the binding energy scale, the B dichroism corresponds to the spin-down projection peak of Mn 3d unoccupied DOS whereas peak A' corresponds to spin-up projection peak of occupied states. Such behaviour of dichroism and appearance of every intensive re-emission contribution at the L_3 X-ray emission line were observed for the first time; it stems, to our opinion, from half-metallic character of Mn 3d DOS in Heusler alloys. The Mn 3d spin-down gap establishes the favourable conditions for increasing of the lifetime of core-excited states that leads to the enhancement of the intensity of the elastic peak, which explains the appearance of non-zero dichroism at photon energy E = 640.5 eV (Figs. 1b, 2a and b).

The high intensity ratio /I(L_2)//I(L_3) at Mn L_2,3 XES excited far above the thresholds (0.89 for NiMnSb, Fig. 1d and 0.76

4. Discussion

The double peak structure revealed in the Mn L_3 XES (Figs. 1b, 2a and b) is a superposition result of normal emission contribution A and elastic X-ray scattering contribution B. As we have already mentioned before, such a giant elastic peak is usually absent in spectra of 3d-metals and alloys, but was observed recently in NiAl XES [12] studied by the resonant X-ray fluorescence spectroscopy that was explained as a band structure effect. According to spin-polarized band structure calculations (Fig. 3), the Mn 3d DOS has half-metallic character for NiMnSb [1,2] and close to that for CoMnSb [13]. In both cases, the Mn 3d DOS have a high spin-up occupation below the Fermi energy and high peak of spin-down unoccupied states in the region of 1–2 eV above the Fermi energy (Fig. 3). From this point, the Mn L_3, L_2 XES of half-metallic ferromagnets, where partial Mn 3d DOS has metallic character for spin-up and insulating character for spin-down projection, are supposed to show some intermediate behaviour.

The X-ray MCD spectra of the 2p → 3d transition can be discussed in terms of the energy-resolved spin-density differences of the valence band. The details of the 3d DOS of transition metals are obscured in their L-emission spectra
for Co₂MnSb, Fig. 2d) for Heusler half-metallic alloys was observed. The effect is conditioned by suppression of fluorescent transitions from 3d states to 2p₃/₂ states having different spin projections. In case of close to 100% spin polarization degree of the Mn 3d states, the simple theoretic estimation gives equal $I(L₂)$ and $I(L₃)$ emission intensities. Neglecting the spin polarization, the same estimation gives 1/2 intensity ratio. The well-known Coster–Kronig decay leads to an additional suppression of $I(L₂)$ intensity, so, the statistic ratio 1/2 is usually less then 0.3 for 3d pure metals [6,10,11]. However, the probability of $2p₃/₂ \rightarrow 3d$ fluorescence transitions in Heusler alloys is decreased as compared, for example, with pure Mn $(I(L₂)/I(L₃) = 0.27$, [14]), because the density of Mn 3d states at the Fermi level for Heusler alloys is essentially smaller than that for pure Mn.

5. Conclusion

In conclusion, we have found MCD effects in X-ray emission of Heusler alloys that indicate strong exchange splitting of the Mn 3d-states with different spin projections. The Mn L₃ re-emission of high intensity is conditioned by the spin-down trap for core-state electron, excited to the valence band. The non-fluorescence transition of this excited electron with energy relaxation is restricted by the presence of the energy gap at the Fermi energy in the spin-down Mn 3d subband. Its leaving out of the excited atom is hampered because of weak hybridization between the Mn 3d states and the nearest neighbourhood. These circumstances lead to an appearance of intensive re-emission contribution at the Mn L₃ XES, resulting in the enhancement of the Mn L₃ XES toward high photon energies in Heusler alloys. The high degree of spin polarization at Mn 3d DOS suppresses the fluorescence transitions from 3d states to 2p₃/₂ states with minority spin, which results in the high $I(L₂)/I(L₃)$ intensity ratio for Mn XES. The Coster–Kronig decay is diminished because of the low density of states at the Fermi energy for Mn 3d DOS of the Heusler alloys, compared to that for the pure manganese.

Acknowledgements

This work was supported by Russian Science Foundation for Fundamental Research (Project 00-15-96575 and 99-02-16268), NATO Linkage Grant, Swedish Natural Science Research Council (NFR) and Göran Gustavsson Foundation in Natural Sciences and Medicine, Deutsche Forschungsgemeinschaft DFG project Br 1184/4 and Bundesministerium fur Bildung und Forschung (BMFB 05SB8MPB8). The single crystal of NiMnSb was supplied by Ch. Hordequien (CNRS) and polycrystalline Co₂MnSb was supplied by Elena I. Shreder (Institute of Metal Physics, Russian Academy of Sciences, Ural Division). The authors are grateful to A. Postnikov for carefully reading the manuscript. Technical assistance of ESRF staff is gratefully acknowledged.

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