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Study of bulk ground state properties of cerium intermetallics by linear dichroism in 4f resonant inelastic X-ray scattering

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Abstract

We have measured polarization effects by 4f resonant inelastic X-ray scattering in the M_5 region of intermetallic compounds of cerium ($CeRh_2$, $CePd_3$, Ce_7Rh_3 , and $CeAl_2$). The experiment was performed using linearly polarized radiation with direction either perpendicular or parallel to the scattering plane. The dichroic effect is strong and depends on the degree of hybridization of the compound. We show that there is a monotonous relationship between the measured dichroism integrated along the emitted energies, and the radius of the cerium ion in different compounds. Since the atomic size of cerium is directly related to its valence, we conclude that the linear dichroism in inelastic X-ray scattering is a bulk-sensitive indicator of the relative weight of the $4f^0$ and $4f^1$ ground state configurations of cerium compounds. © 2002 Published by Elsevier Science Ltd.

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1. Introduction

An important effect connected with the linear polarization of the incident light has been recently pointed out in 4f resonant inelastic X-ray scattering (RIXS) in the soft X-ray range. Linear dichroism has first been calculated and observed at the $L_{2,3}$ thresholds of transition metal oxides (in particular in TiO_2 in Ref. [1]), where a difference in the spectral distribution of the scattered light with resonant excitation was detected upon switching the electric vector of the incident radiation from perpendicular to parallel to the scattering plane. The RIXS spectra (i.e. the spectra as a function of the outgoing photon energy at constant incident photon energy) contain an elastic peak and several inelastic features derived from the multiplet structure of the ground, intermediate and final state. Theory and experiments have shown that, due to the strong directional dependence of

dipole transitions, the intensity of *both the elastic and the inelastic part* of the spectrum are sensitive to the orientation of the linear polarization of the incoming radiation with respect to the direction of the detected scattered radiation. The presence and the size of the dichroic effect depend on the symmetry of the multiplet terms in the ground and in the final state, since the scattering selection rules set restrictions on the accessible final states. Excited final states having the same symmetry as the ground state will obey the same selection rules and polarization dependence so that the corresponding inelastic features can have strong dichroism, as the elastic ones. Thus, the sensitivity of the linear dichroism to the symmetry makes it a promising tool in the investigation of strongly correlated systems, where multiplet splitting is of paramount importance [1,2].

The extension of this approach to rare earths (REs) has been recently suggested by Nakazawa et al. [3] who discussed theoretically the two extreme cases of CeO_2 and CeF_3 within a cluster model based on the Anderson Hamiltonian. The scattering process consists of the resonant excitation of a 3d electron and the consequent de-excitation

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towards a less excited final state via the decay of a 4f electron. The sensitivity of the effect to the initial state symmetry can make this technique very informative in cases where ground state properties are determined by the interaction of different configurations, as it is the case for Ce compounds, whose ground state can be described as $\alpha|f^0\rangle + \beta|f^1\rangle$. Thus, there is a chance that the polarization effect is a new fingerprint of the ground state properties of cerium compounds. Moreover, the information provided by RIXS experiments are related to the bulk electronic states at variance with experiments involving electron beams, like photoemission, where a reasonably high sensitivity to the bulk can be obtained only if very high photon energies are used [4–7].

The present communication contributes with experimental information to this new field where only limited experimental results are at present available to the authors' knowledge.¹ Our focus is on cerium intermetallics that are particularly interesting for the above-mentioned reasons and because they offer the possibility of changing easily the relative weights of the different configurations in the ground state. In fact the ground state of cerium compounds is dictated by the degree of hybridization between the $4f^0$ and $4f^1$ configuration (and to a much smaller extent by the $4f^2$ configuration, which we neglect hereafter in our qualitative discussion). By changing either the partner atom or the stoichiometry, the configuration mixing and thus the valence can be modified: the crystal structure [8] and the electron spectroscopy results [9] will reflect this change. We have studied the linear dichroism effect on a series of cerium compounds with different weights of the $4f^0$ and $4f^1$ states. Our work was aimed at investigating the possible correlation between the measured dichroism and the crystallographic properties that are strictly connected with the valence of Ce and thus with its configuration mixing. We have studied the excitation in the M_3 region, which is a priori the simplest case because it involves the shallower 3d levels. We observe that the effect is very sensitive to the hybridization changes and that excellent correlation with crystallographic data is obtained.

The present results demonstrate the possibilities offered by the new undulators in the third generation synchrotron radiation sources: besides the obvious importance of high flux availability, the complete polarization control allows the exploration of linear dichroism effects without the constraint of changing the scattering plane (which on the experimental side implies a rotation of the analyzing spectrometer output arm as performed in Ref. [1]).

2. Experimental

The measurements were performed with the spectrometer

¹ Limited information on CeRh₃ has been presented at the VUVXIII conference in Trieste, 2001.

described in Ref. [10] equipped with a dedicated monochromator [11], at the new ESRF beamline ID8, where an undulator of the Apple II type [12] allows an easy switching of the linear polarization from vertical to horizontal. The scattering plane of our spectrometer is horizontal and the angle included between the incident and the scattered radiation is 70°.

The experimental geometry is shown in the scheme of Fig. 1, where also the two linear polarizations are specified. The incidence is 10° from the sample surface in order to limit the effect of self-absorption of the outgoing photons (see later). The bandwidths were 1.2 eV for the incident beam and 1.6 eV in the analysis of the scattered photons. The need for maximizing the counting rate dictated the choice of these rather large values, at the expense of a lower resolution. The high-intensity setup is convenient for our discussion largely based on the integrated values of the spectra. In fact, the detailed discussion of the spectral shape was beyond the purpose of the present exploratory investigation.

We have studied the polycrystalline samples of CeRh₂, CePd₃, Ce₇Rh₃, and CeAl₂ (the compounds are listed in the order of decreasing hybridization). The samples were prepared by induction melting from stoichiometric amounts of the pure components under Argon atmosphere and their structure and lattice parameters were checked by X-ray diffraction. Microprobe analysis showed the amount of unwanted phase to be below 1%. The samples were cleaned in situ by scraping with a diamond file. The base pressure of the chamber was in the mid 10⁻⁹ mbar range. Due to the bulk sensitivity, the measurements are not influenced by the uptake from the residual gas over the hours time scale. Nevertheless, for precaution the samples were scraped every 45 min. During each 45 min period a pair of spectra with polarization normal and parallel to the scattering plane were measured. The spectral distribution of the linear dichroism is given by the difference between spectra excited

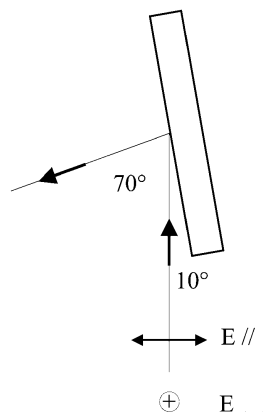


Fig. 1. Experimental lay-out: the scattering plane is horizontal and the linear polarization of the incident light is either in the scattering plane (E_{\parallel}) or perpendicular to it (E_{\perp}).

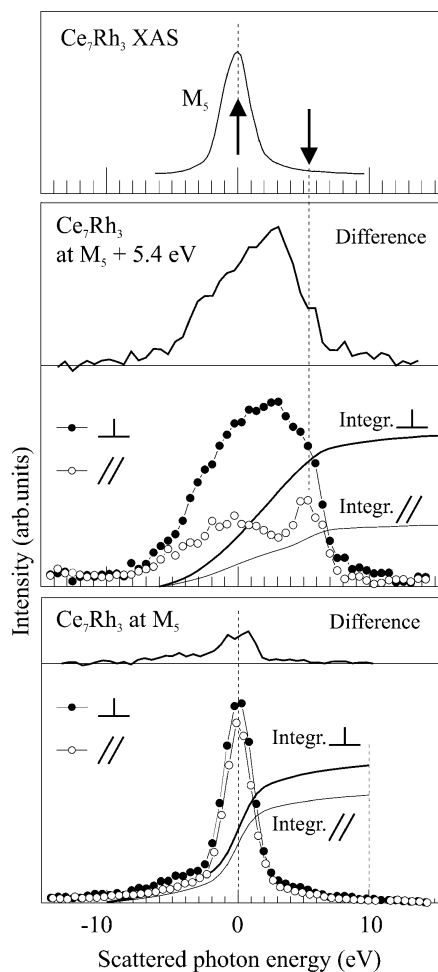


Fig. 2. X-ray linear dichroism spectra of Ce_7Rh_3 . Upper panel: XAS spectrum taken in the Total Electron Yield mode (identical for both polarizations), the arrows indicate the energies at which the scattering spectra were excited. Lower two panels: RIXS spectra excited at the M_5 resonance and 5.4 eV above the resonance. Spectra with filled and hollow dots are excited with polarization normal and parallel to the scattering plane, the thin line is the difference. The scattered energy values are given relative to the elastic M_5 peak. The thin and thick lines superimposed on the RIXS spectra are the integrated spectral values for parallel and perpendicular polarization.

with polarization normal and parallel to the scattering plane. The measured spectra were normalized to the current in the ring and acquisition time. To an excellent approximation this is equivalent to normalizing to the intensity of light arriving onto the sample, as we have verified in separate tests.

3. Results and discussion

The polarization effect is shown for the weakly

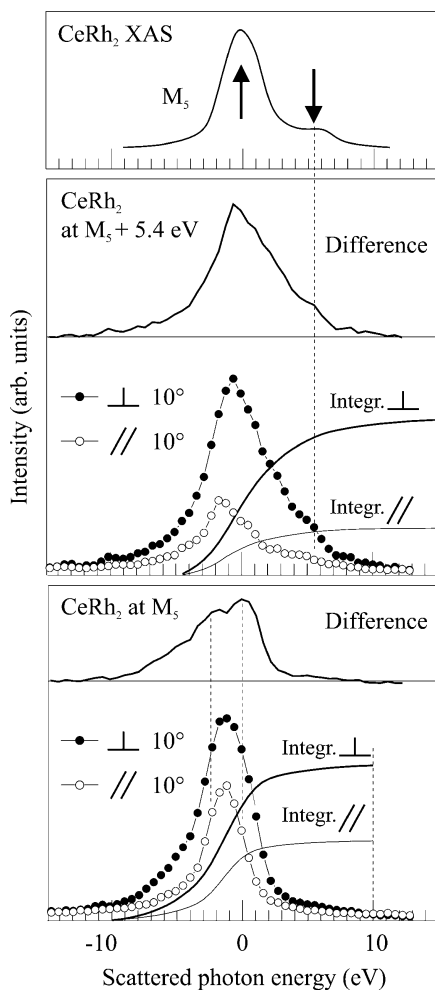


Fig. 3. X-ray linear dichroism spectra of CeRh_2 . Upper panel: XAS spectrum taken in the Total Electron Yield mode (identical for both polarizations), the arrows indicate the energies at which the scattering spectra were excited. Lower two panels: RIXS spectra excited at the M_5 resonance and 5.4 eV above the resonance. Spectra with filled and hollow dots are excited with polarization normal and parallel to the scattering plane, the thin line is the difference. The scattered energy values are given relative to the elastic M_5 peak. The thin and thick lines superimposed on the RIXS spectra are the integrated spectral values for parallel and perpendicular polarization.

hybridized system Ce_7Rh_3 (Fig. 2) and for the strongly hybridized CeRh_2 (Fig. 3) i.e. two compounds that have the same partner (Rh) but different stoichiometry and structure (Ce_7Rh_3 has the hexagonal Th_7Fe_3 structure, CeRh_2 has cubic Laves phase structure). For both compounds we show the results obtained with two excitation energies (see the arrows along the XAS spectrum in the upper panels of Figs. 2 and 3): on the main absorption peak M_5 , and at 5.4 eV above this peak, where the well-known absorption satellite (connected with the $4f^0$ component in the ground

state) is seen in strongly hybridized systems. The scattered photon energies are given relative to the main RIXS peak measured in Ce_7Rh_3 with M_5 excitation. In the case of Ce_7Rh_3 the peak of the spectrum obtained with M_5 excitation is elastic. In CeRh_2 the RIXS peak with M_5 excitation appears at outgoing energies slightly lower than the elastic part, due to the superposition with the strong inelastic contributions excited within the incident band-pass. The values of the integrated emitted intensities as a function of energy are shown together with the RIXS spectra.

The measured dichroism is strong in both the samples and depends upon the incident photon energy. It is worthwhile underlining that, as predicted ([3]), the effect is well seen in polycrystals, as in our case, so that the effect has a very wide potential field of application. In a polycrystal one averages over the orientation of the crystal field but this does not have a great effect since the crystal field is known to be rather weak in REs. The anisotropy in the RIXS is created not by the crystal field but by the existence of a scattering plane. In XAS, where the scattering plane is not defined, the effect is not observed within the sensitivity of the Total Electron Yield measurements (for this reason the XAS spectra of the figures apply to both polarization directions). Also the scattering angle dependence is not critical at least in polycrystals, where possible effects entering the cross-section and connected with crystal symmetry are ruled out. In fact calculations in SO_3 symmetry of the cross-section dependence on the orientation of the incident polarization and on the scattering angle [3] indicate that a scattering angle of 70° results in a minor reduction of the dichroic effect.²

The results of Figs. 2 and 3 show two important facts:

- (i) The dichroism strongly depends on the nature of the compound and is larger in CeRh_2 than in Ce_7Rh_3 . This is clearly seen by comparing the curves representing the integrated values for the two polarizations: in the case of Ce_7Rh_3 the integrated value of the spectrum with polarization parallel to the incident plane (hollow dots) represents a larger fraction of the spectrum with normal polarization (black dots) than in the case of CeRh_2 so that the dichroism is bigger in the latter case. This is in qualitative agreement with the theoretical suggestion that the dichroism should be stronger in more strongly hybridized systems [3]. In fact, in the model calculation on CeO_2 , when the incident polarization is normal to the scattering plane there is a complete suppression of the elastic peak and of those inelastic transitions that reach final states sharing the ground state symmetry. In CeRh_2 the dichroism shows two clear features and a long tail at lower energies reminiscent of the predictions for CeO_2 .
- (ii) The dichroism is very much dependent on the excitation energy and is amplified by exciting in the satellite

² Note that the angle in the experiment could not be put at 90° since the apparatus is tailored to the study of effects such as those of Ref. [13] which do not exist at 90° .

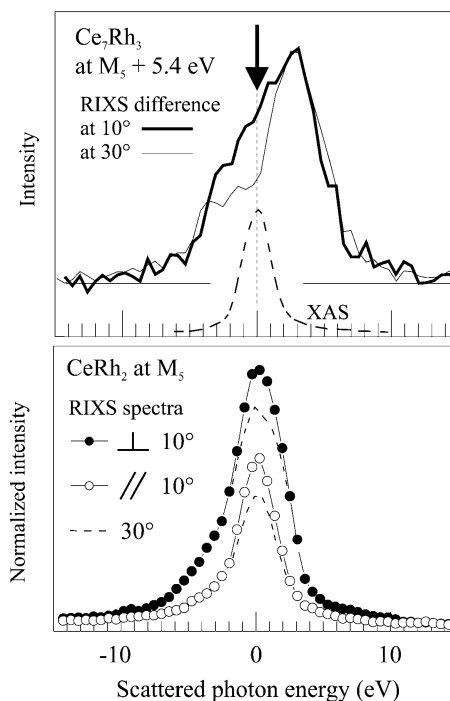


Fig. 4. The effect of self-absorption is shown by comparing spectra measured at two different angles of incidence (10° and 30°) with respect to the sample surface. Lower panel: modification of the RIXS spectral shape in the case of CeRh_2 excited on the M_5 peak, for two different incidence angles: the spectra plotted with filled and hollow dots are measured at 10° , with polarization perpendicular and parallel to the scattering plane, the dashed lines are the corresponding spectra measured at 30° .³ Upper panel: the thin and thick lines are the difference spectrum (dichroism) for Ce_7Rh_3 excited above the M_5 peak with two different angles of incidence. The M_5 XAS spectrum (dashed line) indicates that the spectral modification is related to absorption at the M_5 edge, taking place along the exit path.

region above M_5 where, as it is well known, the contribution from the $4f^1$ configuration in the intermediate state (connected with the $4f^0$ in the ground state) is emphasized. This is supported by the calculations of CeO_2 excited on the M_5 satellite [3] showing that the spectrum is dominated by inelastic components with a larger dichroism than the elastic components.

Before describing the correlation between experimental results and crystallographic data, it is important to illustrate how strongly self-absorption can distort the measurement of

³ In all spectra of Fig. 4 the results at 10° and 30° are normalized by superimposing the spectra in the tail region where the self-absorption is surely very low because the energy is far from the M_5 resonance. This rescaling is necessary since the collection efficiency of the X-ray is necessarily different in the two cases due to the different footprint of the beam on the sample.

this polarization effect. The influence of self-absorption will be illustrated by comparing the data obtained with different incidence angles with respect to the sample surface, i.e. with different exit paths of the scattered radiation. The basic information is given in Fig. 4. In the lower panel we compare CeRh₂ results with M₅ excitation, for 10 and 30° incidence angle (the spectra at 30° are given by the dashed lines). The strongest self-absorption occurs at the energy of the M₅ absorption peak and lowers the intensity of the scattered radiation on the main peak of the spectrum measured at 30° with respect to the tail of the curve. Thus the fractional dichroism decreases considerably at 30°. As it is shown, this happens also for CeRh₂, which is a rather diluted sample. Even worse is the situation when the excitation is above M₅: in this case the inelastic part of the spectrum extends over an energy range including the strong M₅ absorption peak, and self-absorption modulates the spectrum generating artifacts. This is very well seen in Ce₇Rh₃ (upper panel of Fig. 4), which is affected by the largest self-absorption being richest in Ce. The heavy solid line is the dichroism measured at 10° and the thin line is the dichroism at 30°. The M₅ absorption spectrum (dashed curve) shown in the figure gives the conclusive evidence that the modification of the spectral shape of the dichroism is due to M₅ absorption along the outgoing path.³ An accurate analysis of the angular dependence allows us to say that 10° incidence limits the distortion of the spectral features to a few percent and that the area of the dichroism (i.e. the integrated dichroism) is influenced to an even smaller extent. This gives the important warning that, unless self-absorption effects are taken into account, no quantitative information can be extracted from this type of experiment. However, working at the required grazing incidence can give rise to intensity loss, since the footprint of the beam on the sample increases and can exceed the acceptance of the spectrograph.

We will now discuss the correlation between the X-ray linear dichroism and the ground state properties of cerium compounds: a good indicator for the valence and hybridization properties is the space available for the Ce ion given by the radius of the equivalent sphere at the cerium site, obtained from crystallographic data [14]. This is an extremely meaningful parameter since the valence of Ce determines the volume available for the ion [15].

The correlation of Fig. 5 is between two quantities both dependent on the valence (i.e. on the configuration mixing). This relation is not necessarily linear due to the non-linear dependence of the overlap integrals on the distance [16].

The radius is expressed in incremental percentage value in a scale having as two extremes the radius of Ce⁴⁺ (0.94 Å given by CeO₂ and taken as zero) and that of Ce³⁺ (1.034 Å given by CeF₃ and taken as 100%). As an indicator of the dichroism we selected the integrated dichroism at a given excitation energy, i.e. a number giving a value averaged over all the individual contributions coming from multiplet terms present in the spectrum. As integrated dichroism we

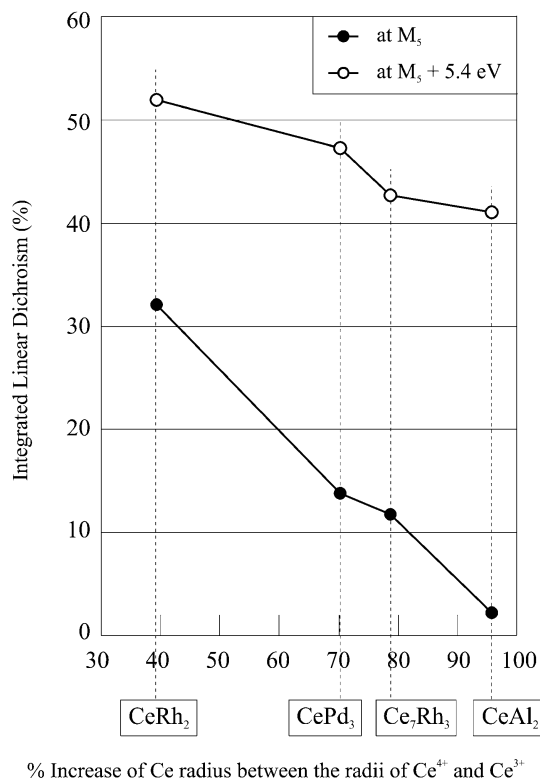


Fig. 5. Integrated dichroism of cerium intermetallic compounds plotted vs. Ce atomic radius. The dichroism is calculated as the difference between the integrals of the spectra with different polarizations, normalized to their sum. On the horizontal scale the size of the Ce atom is plotted in percentage unit between the two extreme values of CeO₂ and CeF₃.

took $(I_{\text{perp}} - I_{\text{par}})/(I_{\text{perp}} + I_{\text{par}})$, where I_{perp} and I_{par} are the integrals of the spectra with perpendicular and parallel polarization. This quantity has been expressed in percentage units. The integrals are taken in the range from -10 to 10 eV of the outgoing photons so that the small signal coming from the 5p states (which have different symmetry and therefore obey different selection rules) is not included.

The integrated dichroism with excitation at M₅ and at M₅ + 5.4 eV are plotted vs. the Ce radius in Fig. 5. The results deserve the following comments:

- (i) The excellent correlation between the dichroic effect and the atomic size, found at both excitation energies, shows the potentiality of RIXS linear dichroism to characterize spectroscopically the degree of hybridization of cerium intermetallics. This good correlation can hardly be under-evaluated, given the difficulties encountered with other spectroscopies that are configuration specific but suffer from surface sensitivity.
- (ii) The correlation shown in Fig. 5 is between two quantities (linear dichroism and ionic radius) that are both dependent on the valence. Each quantity can have a

non-linear dependence on the valence as already evidenced from the very beginning by other high-energy spectroscopies [17]. However, if this dependence is the same, their correlation will become close to linear, as in the present case. Of course, further experimental work on other compounds is needed to assess the details of the correlation and possible exceptions. One of the aims of the present communication is to stimulate this theoretical work: a future computational effort could be useful to discuss the spectral functions and point out possible indicators of the hybridization, more sensitive than the integrated dichroism.

(iii) The variation of the linear dichroism with the radius is stronger when the excitation is set at M_5 than at $M_5 + 5.4$ eV (absorption satellite) although in this last case the absolute value of the dichroism is much stronger, as previously discussed: the slope of a linear regression among the data points is about 2.6 times higher in the case of M_5 excitation. Thus in order to have high contrast in the diagnostic it is convenient to pay the price of having a smaller dichroism and to use lower energy excitation.

In conclusion we have presented an assessment of the RIXS linear dichroism in Ce intermetallics and of its dependence on the ground state properties by comparing systems having different hybridizations. The strong dependence of the M_5 integrated dichroism on the ionic radius and the large value of the dichroism presented here gives a very convincing demonstration of the power of this new spectroscopic approach.

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