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Experimental evidence of pressure-induced suppression of the cobalt magnetic moment in $ErCo_2$

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X-ray absorption spectroscopy (XAS) and x-ray magnetic circular dichroism (XMCD) measurements have demonstrated the modification of the magnetic moment of Co in $ErCo_2$ induced by applying pressure. Co *K*-edge and Er L_2-edge XAS and XMCD spectra recorded under applied hydrostatic pressures up to 4.2 GPa reveal that the modification of the magnetic properties of Co proceeds through two different pressure regimes. At low pressure, the Co atoms show an ordered magnetic moment induced by the effective field created by the Er sublattice. The Co moment progressively diminishes as the applied pressure increases, but it is not canceled for applied pressures of up to 4.2 GPa. The results show that the pressure mainly affects the Co subsystem without affecting the magnetism of the Er sublattice.

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The intermetallic RCo_2 compounds (*R* stands for rare-earth elements) have been widely studied from both experimental and theoretical viewpoints.[1] The Co 3*d* band states in the RCo_2 compounds appear near the critical conditions for Co moment formation and, consequently, they can be regarded as model materials for itinerant electron metamagnetism (IEM).[2] The RCo_2 compounds in which *R* is nonmagnetic (YCo_2, $LuCo_2$) are exchange-enhanced Pauli paramagnets. At low temperatures, these compounds are rendered ferromagnetic by applying a critical magnetic field $B_c \sim 70$ T,[3] as a consequence of the sudden splitting of the majority- and minority-spin 3*d* subbands of Co. By contrast, when the *R* is magnetic, the Co subsystem is magnetically ordered, $\mu_{Co} \sim 1\mu_B$, in zero external magnetic field due to the effect of the molecular field B_{eff} created by the *R* moments acting on the Co sites.[4]

$ErCo_2$ orders ferromagnetically at $T_C \sim 32$ K. This first-order magnetic phase transition is accompanied by the appearance of a Co moment. As the Er 4*f* magnetic moments ferromagnetically order, the exchange field is large enough to favor IEM and to induce magnetic ordering of the Co sublattice. The effective field B_{eff} acting upon the Co subsystem decreases with increasing external field. In the case of $ErCo_2$ the collapse of the Co moment takes place for an applied magnetic field of 52 T.[5] Moreover, the B_{eff} acting on the 3*d* electrons can be strongly reduced by substituting the Er ions with nonmagnetic Y,[6] or by applying pressure.[7] In the latter case, it has been proposed that the IEM transition is suppressed by applying a critical pressure p_c, due to the increase of the critical field for the IEM as pressure increases.[8]

Despite the great body of research performed on the RCo_2 systems, little experimental work is available on the effect of pressure on the IEM transition. In recent years, Hauser *et al.*[9] and Syshchenko *et al.*[10] have studied the effect of pressure in $ErCo_2$ through the analysis of the electrical-resistivity anomalies in the vicinity of T_C. The observed deviation from linearity of the pressure dependence of T_C has been interpreted in terms of a progressive suppression of the Co moment while the Er moment is not modified by the effect of pressure. Then, it has been proposed that for $p \sim 2.5$ GPa the itinerant *d* subsystem is destabilized and the Co moment near disappears as B_{eff} becomes ineffective in inducing the IEM.

Unfortunately, no direct information regarding the behavior of both Er and Co sublattices can be obtained separately. In this Rapid Communication, we report a combined x-ray absorption (XAS) and x-ray magnetic circular dichroism (XMCD) study performed at the Co *K* edge and at the Er L_2 edge in $ErCo_2$ as a function of the applied pressure. Because of the atomic selectivity of these techniques, this approach furnishes a disentangled magnetic characterization of the two Er and Co sublattices. As a result, the dependence of both μ_{Er} and μ_{Co} on the applied pressure has been determined separately.

$ErCo_2$ sample was prepared by arc-melting the pure elements under an Ar protective atmosphere. The ingot was annealed in evacuated quartz tubes at 850 °C for one week. Structural characterization was performed at room temperature by means of powder x-ray diffraction. The sample is single phase showing the $MgCu_2$-type (*C*15) Laves structure ($Fd3m$ space group) with a lattice constant $a=7.157$ Å. Magnetization measurements were performed by using a commercial superconducting quantum interference device magnetometer (Quantum Design MPMS-S5) in magnetic fields up to 5 T. The sample was zero-field cooled down to 4.2 K and the magnetization vs temperature $M(T)$ curves were recorded on heating. The Curie temperature $T_C=32$ K was determined at the inflection point of the $M(T)$ curve measured upon an applied field of 0.1 T. The magnetization measured at 5 T is $M_{5\ T}=7.2\mu_B$/f.u. Assuming the free-ion value ($9\mu_B$) for the erbium moment, the corresponding Co moment is $\mu_{Co}=0.9\mu_B$ at 5 T.

XMCD experiments under high pressure were carried out using the helicity-reversal method at the beamline BL39XU of the SPring8 Facility.[11] XMCD spectra were recorded in the transmission mode at both the Co *K* edge and Er $L_{2,3}$ edge under hydrostatic pressures of up to 4.2 GPa. For these measurements a tiny diamond anvil cell, 23.8 mmϕ $\times$47 mm, was utilized and inserted into a superconducting electromagnet, the pressure in the sample being monitored by the ruby fluorescence method. The XMCD spectra were

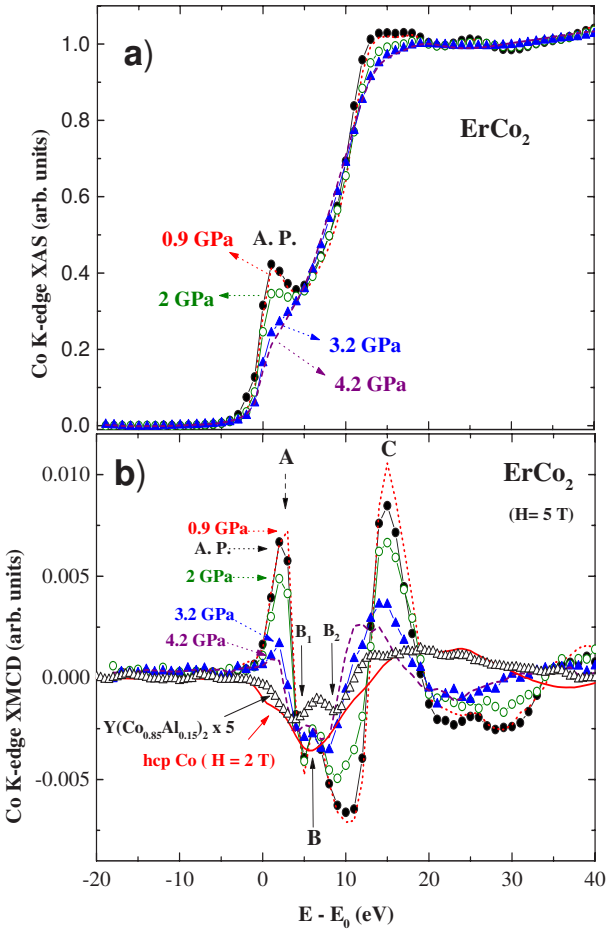

FIG. 1. (Color online) (a) Comparison of the normalized Co *K*-edge XAS spectra of $ErCo_2$ recorded at ambient pressure (black, ●), $p=0.9$ GPa (red, dotted line), 2 GPa (green, ○), 3.2 GPa, (blue, ▲), and 4.2 GPa (purple, dashed line). (b) The XMCD spectra of $ErCo_2$ recorded as a function of the applied pressure (same legends as above) are compared to those of $Y(Co_{0.85}Al_{0.15})_2$ (black, △) and hcp Co (red, solid line) recorded at ambient pressure. In all the cases the applied magnetic field was $H=5$ T, with the exception of hcp Co for which $H=2$ T was used.

recorded at $T=5$ K and under the action of an applied magnetic field of 5 T. The XMCD spectrum corresponds to the spin-dependent absorption coefficient obtained as the difference of the absorption coefficient $\mu_c=(\mu^- - \mu^+)$ for antiparallel, μ^-, and parallel, μ^+, orientations of the photon helicity and the magnetic field applied to the sample. The absorption spectra were analyzed according to standard procedures: the origin of the energy scale, E_0, was chosen at the inflection point of the absorption edge and the spectra were normalized to the averaged absorption coefficient at high energy.

Figure 1 reports the Co *K* edge XAS spectra of $ErCo_2$ recorded as a function of the applied pressure. At ambient pressure the Co *K* edge spectrum is characterized by a steplike structure at the threshold. In this region, the absorption spectrum carries information about the electronic state of the absorbing atom as the photoelectron probes the unoccupied ground-state local and partial density of states.[12] The cancellation of the IEM transition in $ErCo_2$ upon applying pressure is associated with the abrupt change of the density of Co 3*d* states at the Fermi energy E_F. Consequently, it is expected that this phenomenon will be reflected in both the shape and intensity of the shoulderlike feature of the Co *K*-edge spectrum. As shown in Fig. 1(a), no significant variation of the whole XAS spectrum recorded at ambient pressure (AP) is observed upon applying a 0.9 GPa pressure. However, the spectrum markedly changes for applied pressures higher than $p\sim 1$ GPa. In the case of $p=2$ GPa, the height of the threshold peak ($E-E_0=1$ eV) is reduced by 20% with respect to the AP one. For $p=3.2$ GPa, the threshold feature has changed from the well-defined peak found at AP to a shoulderlike spectral shape and, in addition, its intensity is reduced by 40% with respect to the AP data. For further increase of the applied pressure, $p=4.2$ GPa, the XAS spectrum remains unaltered. Therefore, as pressure increases the intensity of the shoulderlike feature decreases and the rising edge is shifted toward higher energies. This spectral feature is originated by the large *p*-*d* hybridization of the conduction bands at the Fermi level.[13] Then, the observed reduction of its intensity indicates that the density of empty *p* (*d*) states above the Fermi energy decreases, while the shift of the Co *K*-edge threshold can be related to that of the Fermi level. Both experimental findings reflect that the hybridization among the Co conduction states and those of the neighboring atoms is strongly modified by the effect of pressure.

The differences found in the near-edge region confirm that applying pressure exerts a large electronic perturbation in the system. Moreover, these results suggest that $ErCo_2$ evolves through two different magnetic regimes as a function of the applied pressure: (i) AP and $p\leq 2$ GPa [low pressure (LP)], and (ii) the high-pressure (HP) regime for $p\geq 3$ GPa. This scenario is in agreement with that derived, at the macroscopic level, by studying the pressure dependence of the resistivity and T_C.[9,10] To account for this behavior it has been proposed that (i) the magnetic properties of the Er sublattice are basically not modified by the effect of pressure, and (ii) the Co subsystem suffers an inverse IEM transition as pressure increases because the effect of B_{eff} is counteracted by the applied pressure. If this is the case, pressure suppresses the splitting of the 3*d* spin-polarized band and the Co subsystem becomes similar to that in the YCo_2 and $LuCo_2$ enhanced paramagnets.

Trying to disentangle the effect of pressure on both Er and Co sublattices, we have studied the pressure dependence of the XMCD signals recorded at both the Co *K* and Er *L* edges. The pressure dependence of the Co *K*-edge XMCD of $ErCo_2$ is shown in Fig. 1(b). For both AP and $p=0.9$ GPa, the spectra are similar and markedly different, in both shape and amplitude, from those recorded in the HP limit (≥ 3 GPa). The XMCD spectrum recorded at $p=2$ GPa is similar to those in the LP regime and only the amplitude, but not the shape, is mainly affected. The correlation between the shape of the XMCD and the Co magnetic state has been performed by taking into account previous results obtained for *RM* compounds (*M* being a 3*d* transition metal).[14,15] These works have unambiguously determined that there is a rare-earth contribution to the transition metal *K*-edge XMCD spectrum reflecting the magnetic state of the *R* atoms. This is illustrated in Fig. 1 where the XMCD spectra of $ErCo_2$ and hcp Co are compared. The XMCD spectrum of hcp Co shows a

main broad negative peak (B) extending over the first 17 eV. By contrast, the spectrum of AP $ErCo_2$ shows two prominent peaks at ~2 (A) and 15 eV (C) above the edge. It should be noted that the sign of the XMCD signals is referred to the total magnetization of the system. In the case of $ErCo_2$, the direction of the magnetization is parallel to the Er magnetic moment μ_{Co} being ferrimagnetically coupled to μ_{Er}. Therefore, the sign of the Co contributions to the Co K-edge XMCD should be opposite for hcp Co and $ErCo_2$.

As the applied pressure increases, the amplitude of the $ErCo_2$ XMCD signals decreases. This result suggests that the effect of Er on the Co K edge is progressively softened by the effect of pressure as the hybridization among the Co conduction states and those of the Er neighboring atoms weakens. Moreover, the shape of the XMCD spectra markedly changes as the applied pressure lies in the HP regime. There is dramatic reduction of the intensity of peaks A and C and the shape of the negative dip evolves so as to resemble the XMCD spectrum of the weakly itinerant ferromagnetic $Y(Co_{0.85}Al_{0.15})_2$ compound, which shows two well-resolved negative peaks (B_1 and B_2) in the same energy region. These results indicate that for high applied pressures the influence of the Er magnetic moment on the Co K-edge XMCD is significantly weakened. This result is in agreement with the R-Co-R exchange channel becoming less effective to induce the IEM as the effect of B_{eff} is counteracted by the applied pressure.[10] Indeed, previous theoretical calculations have reported a sudden drop of the Co moment from $\sim 0.78\mu_B$ to $\sim 0.1\mu_B$ induced by the applied pressure.[10]

In order to verify these results and to get information about the effect of the pressure on the Er magnetic moment a similar XMCD study has been performed at the Er L_2 edge. As shown in Fig. 2, the main effect of pressure is to increase the height of the main absorption line (white line). The intensity of the white line is directly related to the localization of the 5d states.[16] Consequently, this result reflects the progressive localization of the Er 5d states at increasing pressure, resulting in the decrease of the hybridization between the Er and Co conduction states. Further information on the pressure-induced modification of the Co magnetic moment can be obtained from the comparison of the XMCD spectra recorded as a function of the applied pressure and for $ErAl_2$. As shown in Fig. 2 the L_2-edge XMCD of $ErAl_2$ exhibits a main negative peak and a positive peak of lower intensity centered, respectively, at ~1 and ~7 eV above the edge. In the case of the $ErCo_2$ signals the main negative feature is strongly modified, in both shape and intensity, with respect to that of $ErAl_2$. The amplitude of the $ErCo_2$ XMCD at AP is about half that of $ErAl_2$. This difference cannot be accounted for in terms of the reduction of the Er magnetic moment and is due to the existence of an extra contribution at the rare-earth L_2-edge XMCD spectrum due to the transition metal.[17] Accordingly, the differences between the XMCD spectra of $ErCo_2$ and $ErAl_2$ recorded under the same experimental conditions are due to the magnetic contribution of the Co atoms, even when Er is probed.

This additional contribution, thought to be proportional to μ_{Co},[17] can be extracted from the $ErCo_2$ XMCD spectra by subtracting the $ErAl_2$ one. The result of applying this procedure is shown in the lower panel of Fig. 2. The difference,

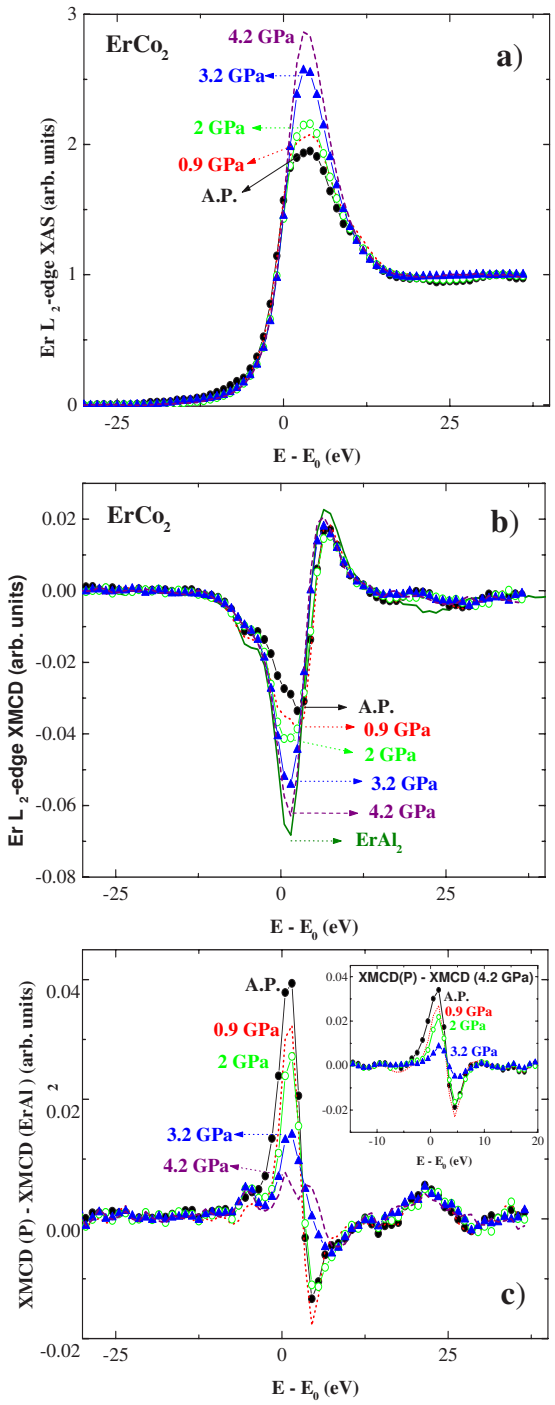

FIG. 2. (Color online) (a) Comparison of the normalized Er L_2-edge XAS spectra of $ErCo_2$ recorded at ambient pressure (black, ●), p=0.9 GPa (red, dotted line), 2 GPa (green, ○), 3.2 GPa (blue, ▲), and p=4.2 GPa (purple, dashed line). (b) The same comparison is shown for the Er L_2-edge XMCD spectra recorded at T=5 K and an applied magnetic field H=5 T. The Er L_2-edge XMCD spectrum of $ErAl_2$ recorded at ambient pressure under the same experimental conditions is also shown (olive, solid line). (c) Comparison of the signals obtained after subtracting the XMCD spectrum of $ErAl_2$ from that of $ErCo_2$ recorded as a function of the applied pressure. In the inset a similar comparison is shown but subtracting the XMCD spectrum of $ErCo_2$ recorded at the maximum applied pressure.

$\mathrm{XMCD}|_{\mathrm{ErCo_2}}(p) - \mathrm{XMCD}|_{\mathrm{ErAl_2}}(\mathrm{AP})$, shows a single positive peak whose intensity decreases as the applied pressure increases. The shape of the extracted Co contribution is the same for $p \leq 2$ GPa. However, for higher pressures $p=3.2$ and 4.2 GPa, there is a sudden drop of the intensity and the shape of the extracted signal is modified. The decrease of the intensity might be related to a weaker contribution of Co as the magnetic moment of Co decreases and the Er-Co hybridization weakens. This behavior is in agreement with that observed at the Co K edge. We have estimated the reduction of μ_{Co} from the XMCD signals in the following way. We have assumed that (i) the intensity of the extracted Co contribution is proportional to μ_{Co}, and (ii) the main positive resonance of the Er L_2 edge XMCD (Fig. 2, middle panel) is exclusively due to Er and proportional to μ_{Er}. By assuming that $\mu_{\mathrm{Er}} = 9\mu_B$ and μ_{Co} is $0.9\mu_B$ at AP, we find a linear decrease of μ_{Co} as pressure increases while the magnetic moment of Er remains unchanged (see Fig. 3). The values derived for μ_{Co} have been compared in Fig. 3 to the pressure dependence of T_C.[9,10]

The comparison suggests, as in the Co K-edge case, that for pressures above $p=3$ GPa the effect of the Er B_{eff} on the Co sites is counteracted by the applied pressure. However, the IEM transition is not suppressed, and an ordered Co moment is still present in the HP regime. From extrapolation of the linear trend observed, the Co moment would be $0.18\mu_B$ at $p=4.2$ GPa and the critical pressure for the complete cancellation of μ_{Co} would be 5 GPa. It should be noted that the observed modification of both XAS and XMCD spectral shape in the high-pressure regime indicates the modification of the electronic structure of the system. If this is the case, the assumed proportionality between the extracted signals and the Co moment would no longer be valid and, consequently, the values derived for the HP regime should be considered with some caution.

In summary, we have reported here a combined XAS and XMCD study performed at both the Co K edge and the Er L_2 edge of $ErCo_2$ as a function of the applied pressure. The results show that the pressure mainly affects the Co subsystem without affecting the magnetism of the Er sublattice. The Co moment is not canceled for applied pressures of up to 4.2 GPa. This XMCD study will contribute to a better understanding of the nature of the IEM metamagnetic transition in itinerant-electron R-Co systems and in the modification of the effective field acting on the Co subsystem by applying hydrostatic pressure.

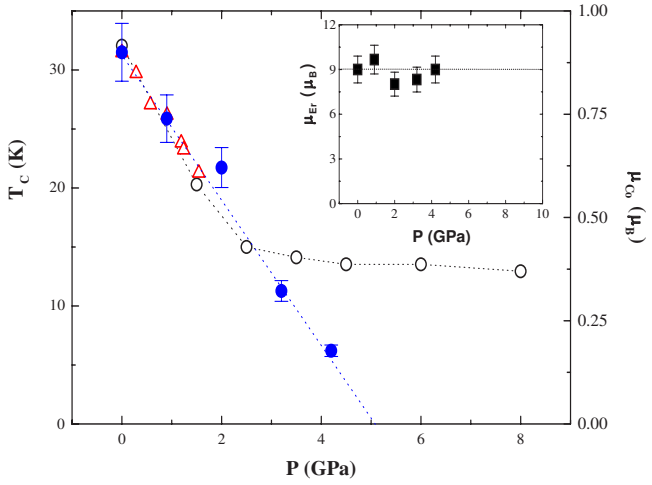

FIG. 3. (Color online) Comparison between the pressure dependence of T_C of $ErCo_2$: data are taken from Ref. 9 (red, △) and Ref. 10 (black, ○), and of the Co magnetic moment derived from the Er L_2-edge XMCD spectra (blue, ●). In the inset, the pressure dependence of the Er magnetic moment derived also from the Er L_2-edge XMCD spectra is shown (see text for details).

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