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Report:

X-ray resonant Raman scattering (RRS) from $3d$-electrons in $TbF_3, TbCo_2$, and $Gd_3Fe_5O_{12}$ was recorded at incident energies resonant with their respective L_2 absorption thresholds (In the case of the Tb compounds, spectra were recorded as well around the L_3 absorption edge). The goal of the experiment was twofold: 1) determination of the location and the strength of the quadrupolar $2p \rightarrow 4f$ (E2) excitation channel with respect to the strong dipolar $2p \rightarrow 5d$ (El) channel; 2) observation of changes in the inelastic scattering spectra and the above quantities for the two limit cases of a metallic and an ionic rare-earth compound.

Figure 1 shows representative inelastic scattering spectra, recorded at the indicated incident photon energy in the pre-edge region (L_2 edge for figure la and lb, and L_3 edge for figure lc) as a function of scattered energy $\hbar\omega_2$. In all cases, the spectra are characterized by a main feature, labelled B, a low energy satellite (B^*), and a feature (A) at the high-energy side of feature B. In close analogy to previous RRS studies at the L_3 edges of rare-earth compounds [1,2], comparison of the RRS spectra of the same compounds at the L_2- and L_3 edges in the present study, and theoretical predictions [3], the following assignment can be done: features B and B^* constitute the $3d^9 4f^n 5d^1$ final state multiplet, deriving from dipolar intermediate state excitations of a $2p$ electron into empty $5d$ states. Final state correlation effects between the incomplete $3d$- and $4f$-shells lead to a splitting of this multiplet into two groups B and B^*. Feature A constitutes the $3d^9 4f^{n+1} 5d^0$ final state multiplet, deriving from quadrupolar intermediate state excitations of a $2p$ electron into empty $4f$ states.

The difference between a metallic ($TbCo_2$, dotted line) and an ionic compound (TbF_3, solid line),- displayed in figure lb and lc for the Tb L_2- and L_3 edge, respectively,- manifests itself in a broadening of feature B, reflecting the increased width of the $5d$ band, and, more importantly, in a reduction of the energy difference between the two multiplet families A and B.
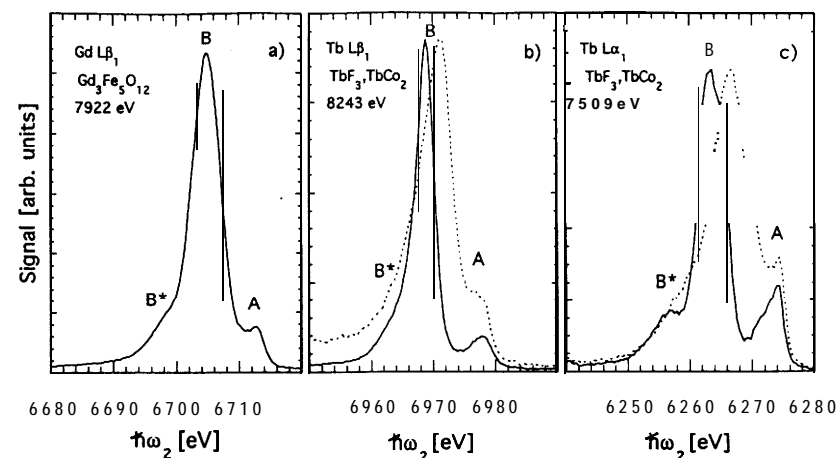

FIG.l: Inelastic x-ray scattering spectra as a function of scattered photon energy $\hbar\omega_2$. The incident photon excitation energy is located in the pre-edge region and its value is indicated in the upper left of each panel. **a)** $Gd_3Fe_5O_{12}$, L_2 edge, $3d_{3/2} \rightarrow 2p_{1/2}(L\beta_1)$ radiative decay channel. b) TbF_3 (solid line) and $TbCo_2$ (dotted line), L_2 edge, $3d_{3/2} \rightarrow 2p_{1/2}(L\beta_1)$ radiative decay channel. c) TbF_3 (solid line) and $TbCo_2$ (dotted line), L_3 edge, $3d_{5/2} \rightarrow 2p_{3/2}(L\alpha_1)$ radiative decay channel. The spectra in panel b) and c) are normalized to the the same peak intensity.

The intensity evolution of features A and B as a function of incident photon energy was determined from the complete set of RRS spectra, and by constant final state scans (incident and scattered photon energy are scanned together, while the energy transfer is kept fixed to the value, corresponding to the excitation energy of feature A and B, respectively), thus allowing to determine the exact resonance condition and the strength of the El- and E2 excitation channels. Taking the energy position and the strength of the dipolar excitation channel I_{E1} as reference, we obtain for the E2 excitation channel:

1) L_2 edge
$Gd_3Fe_5O_{12}$: AE = -6.5 eV; $I_{E2}/I_{E1} = 0.006$
TbF_3: AE = -8.0 eV; $I_{E2}/I_{E1} = 0.009$
$TbCo_2$: A E = -6.5 eV; $I_{E2}/I_{E1} = 0.009$

2) L_3 edge
TbF_3: AE = -8.5 eV $I_{E2}/I_{E1} = 0.025$
$TbCo_2$: A E = -6.5 eV $I_{E2}/I_{E1} = 0.024$

The complete set of data for the two Tb compounds reveals that the $2p \rightarrow 4f$ excitation is observed at the same incident energy, and that the E2/El intensity ratio is identical within the experimental error, whereas the energy of the El excitation channel, as expected, depends on the nature of the chemical bond.

In summary, our results demonstrate the existence of a quadrupolar excitation channel as well at the L_2-edges of rare-earth compounds, and suggest a similar systematics as for the L_3-edges [2], i.e. increasing energy separation between E2- and El channel with increasing atomic number in the rare-earth series. Moreover, these systematics are modified, as we show for the case of an ionic and a metallic Tb compound.

[1] M.H. Krisch, C.C. Kao, F. Sette, W. Caliebe, K. Hämäläinen, and J.B. Hastings; Phys. Rev. Lett. 74, 4931 (1995). [2] F. Bartolome, J.M. Tonnerre, L. Seve, D. Raoux, J. Chaboy, L.M Garcia, M. Krisch, and C.C. Kao; Phys. Rev. Lett. 79, 3775 (1997). [3] M. van Veenendaal, Phys. Rcv.B, (1997).