Comment on "Dipolar Excitations at the L_{III} X-Ray Absorption Edges of the Heavy Rare-Earth Metals"

Over the past two decades, new scattering and spectroscopy techniques such as x-ray magnetic circular dichroism (XMCD), x-ray resonant magnetic scattering (XRMS), and, most recently, x-ray resonant interference scattering (XRIS) have provided important new insights into the magnetic and electronic structures of materials. All of these techniques are rooted in the dichroic cross section involving resonances near the x-ray absorption edges of elements. In a recent Letter, Brown *et al.* [1] combined XRIS measurements with first-principles scattering theory and an atomic-like model to reexamine the dipolar ($E1$) or quadrupolar ($E2$) character of features near the L_{III} absorption edges of heavy rare-earth metals. In their modeling of the scattering data, Brown *et al.* [1] did not include radial matrix elements, instead relating the measured asymmetry ratio directly to differences in the unoccupied spin-polarized density of states. Specifically, in the case of Tm, it was necessary for them to invert the calculated XRIS spectrum, with respect to the experimental XRIS data, to obtain reasonable agreement. This motivated their interpretation of the results in terms of a non-Hund's-rule compliant intermediate state. In this Comment, we point out that the radial matrix elements do play an important role in the modeling of dichroic spectra. They can lead to significant shifts in the spectral weight of features calculated from only the spin-polarized density of states and, in some instances, inversion of the dichroic spectrum.

First, in contradiction to Brown *et al.'s* [1] claim that the radial matrix elements vary slowly over the energy range of interest, first-principles band calculations have shown that the energy dependence is quite strong, varying by a factor of 2 over the energy range of interest for rare-earth metals [2,3]. The lower energy occupied $5d$ states have bonding character, while the empty $5d$ states above the Fermi energy develop antibonding character near the top of the of the d bands. Here, the $5d$ radial functions are more strongly localized and have larger dipole matrix elements with the $2p$ core states. Perhaps most importantly, differences in the dipole matrix element between the spin-up and spin-down radial wave functions and the $2p$ state can profoundly change the nature of the resonance spectra, leading to an inversion of the features as compared to calculations using only the unoccupied density of states, as done by Brown *et al.* . For example, Fig. 1 shows the calculated $E1$ contribution to the XMCD spectrum for Tm from the first-principles band calculations found in Ref. [2]. By including the matrix elements in the calculation, inversion of the theoretical curve for Tm, with respect to the experimental data, is not required. We also note that there is reasonable agreement between the positions (and signs) of features in Fig. 1 and the Tm XRIS data published by Brown *et al.* [1] without the need for any shift in the energy scale to superpose the peaks as was done in Ref. [1]. We wish to emphasize here that the matrix element effects can not be ignored in a comparison between theory and experimental data from XRMS, XMCD, or XRIS measurements [4,5].

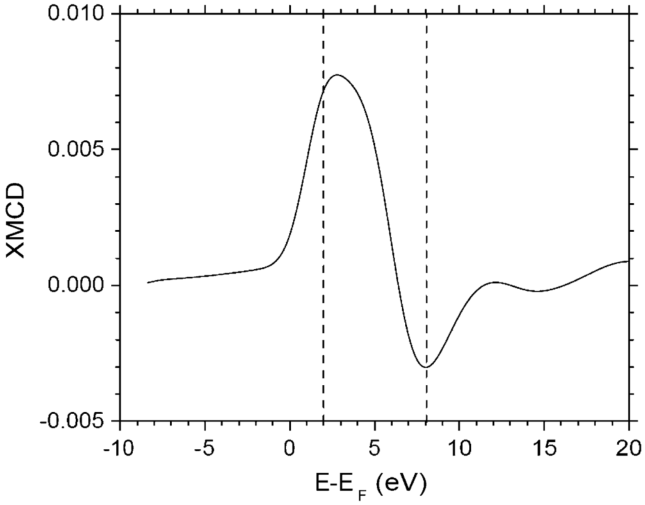

FIG. 1. The $E1$ contribution to the XMCD spectrum for Tm metal calculated from first-principles band theory including radial matrix elements as described in Ref. [2]. The vertical dashed lines refer to the positions of features A and B in Figure 1 of Ref. [1].

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