Collaborative Inelastic X-ray Scattering and First Principles Theory Investigations of the Dynamical Electronic Structure of Transition Metals and Transition Metal Oxides

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Introduction

Electronic interactions play central roles in determining the physical properties of materials, including all transport-related phenomena. Although both long- and short-range electron correlations have been the subject of intense theoretical investigation, a full understanding of these effects and their interplay with the band structure of real materials remains a significant challenge. Advances in inelastic x-ray scattering (IXS) measurements of dynamical electronic phenomena by using third-generation synchrotron x-ray sources have occurred concurrently with recent developments in *ab initio* electron density-response methods for periodic crystals [1]. The exploitation of the direct linkage between density response and IXS through the dynamical structure factor as a function of wave vector and frequency represents a promising framework for achieving a fundamental understanding of electron correlations. IXS measurements have been made of the energy loss spectra for transition metals and transition metal oxide materials by using the UNI-CAT beamline at the APS. Analyses of these measurements by using first-principles time-dependent density functional theory (TDDFT) calculations have shown that detailed information can be obtained on electronic excitations. The analyses have further shown that the basic dynamical electronic physics is already contained in the random-phase approximation (RPA) — even for correlated electron systems such as transition metals — if crystal local field effects are included.

Methods and Materials

Nonresonant IXS measurements of the dynamical structure factor $S(\mathbf{q},\omega)$ provide a direct measure of the dynamical electronic response of materials through the relationship:

$$S(\mathbf{q},\omega) = -2\hbar V \,\mathrm{Im}\,\chi(\mathbf{q},\omega), \qquad (1)$$

where the density response $\chi(\mathbf{q},\omega)$ is obtained through first-principles computations with reciprocal space resolution corresponding to a volume V, including the full band structure of the material [1]. The general application of this direct linkage of experimental measurements with first-principles theory and computations (with no adjustable parameters) has been restricted by difficulties in scaling IXS measurements to absolute units for non-free-electron metals. We have developed a simple but important and previously unused procedure [1] for obtaining absolute intensity measurements on arbitrary materials. Using this procedure, IXS measurements of $s(\mathbf{q},\omega) = S(\mathbf{q},\omega)/V$ on arbitrary materials are scaled to absolute (i.e., *f* sum-rule) units by performing an absolute measurement on Al and scaling by the ratio of absorption coefficients for Al and the material to be measured. IXS measurements of the dynamical structure factor $s(\mathbf{q},\omega)$ for the single-crystal transistion metals Sc, Cr, and Ni and the band insulator TiO_2 have been made at UNI-CAT beamline 33-ID at the APS. The measurements were made for a variety of momentum transfers q ranging from 0.6 to 4 A^{-1} by using the ~1-eV energy resolution high-heat-load Si 111 incident beam monochromator and a spherically bent Ge analyzer operating in the near-backscattering geometry. Energy loss spectra were measured over a range of 3 to 60 eV.

Results and Discussion

Figure 1 shows typical measurements and TDDFT calculations for Cr at wave vectors of 2.0 and 3.5 A^{-1}. The general form of the IXS measurements made on transition metals are similar to those discussed in earlier reports [2, 3] on Cr and Ti. A comparison of the present measurements for Cr with first-principles measurements in Fig. 1 shows that both RPA and adiabatic local density approximation (ALDA) approximations provide rather good representations of the measured response for energies below the M absorption edge at 40 eV. This result is typical for IXS measurements that we have made on Sc, Cr, and Ni for wave vectors ranging from 0.6 to 4 A^{-1}. Considering the fact that the comparison in Fig. 1 between the measurements and calculations is in absolute units, with no adjustable scaling parameters, this result is remarkable and could not have been predicted considering the localized nature of the *d*-electrons in these materials and the LDA band structure. Although RPA reflects the essential dynamical electronic physics for these metals, it is important to note that the inclusion of many-body local

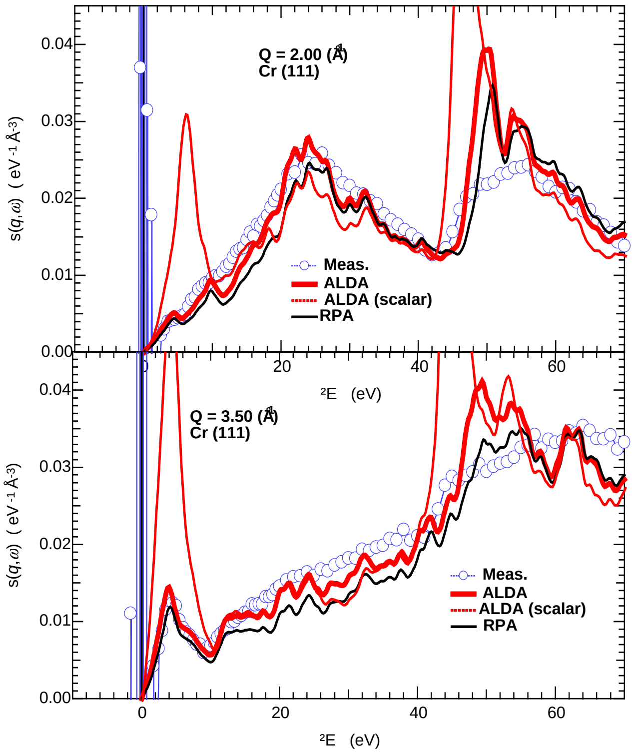

FIG. 1. IXS measurements (open circles) as a function of energy loss ΔE for [111]-oriented Cr compared with RPA (solid black line), ALDA (thick red line), and ALDA scalar (thin red line) calculations.

field effects, as contained in ALDA, does provide a better description of the loss spectra, and that understanding many-body effects will play an essential role in achieving a full understanding of the dynamical electronic structure.

On the other hand, comparing the ALDA scalar calculations (i.e., without crystal-field effects) with the full ALDA calculations illustrates the fact that the “crystal” local fields make a dramatic impact on the dynamical response, both below 10 eV and above the M edge for both wave vectors. Considering the structure of the spectra below 10 eV in Fig. 1, dissection-analyses of the computations indicate that the sharp peak at ~4 eV for 3.5 A^{-1} is due to *d*-to-*d* transitions, involving narrow *d* complexes lying below and above the Fermi surface. Such direct *d-d* excitations are inaccessible to optical absorption because of selection-rule (parity) considerations, which do not apply to the x-ray (Thomson) scattering case. These results underscore the importance of IXS for measuring beyond the optical **q** ~0 limit for investigations of dynamical electronic structure in such materials.

These results illustrate the capability to “dissect” first-principles computations in order to identify the origin of experimentally observed features in energy loss spectra [4]. In view of the rather limited agreement between the measured and calculated spectra at the *M* edge, it is apparent that either (or both) the local density and the adiabatic approximations underpinning TDLDA break down. This *M*-edge result is not entirely unexpected, considering the difficulty of LDA band structures in handling semicore electrons.

IXS measurements on the transition metal oxide TiO_2 indicate (similar to the case for the transition metals in Fig. 1) that RPA calculations provide a rather good first approximation to the measured features in the loss spectrum. The results also show that crystal local fields impact the excitation spectra in the oxide even more dramatically than the spectra in the transition metals. Considering the results for transition metals and TiO_2, a message is beginning to emerge that RPA and a proper ground state provide a significant part of the physics for transition metals and band insulators, provided the band structure and crystal local fields are included.

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