

Core Hole Effects in Resonant Inelastic X-Ray Scattering of Graphite

In a recent Letter [1], Carlisle *et al.* reported dispersion effects in resonant inelastic x-ray scattering (RIXS) from graphite [2]. RIXS is a coherent process involving absorption and reemission of soft-x-ray photons that occurs near a core-excitation threshold, and is analogous to x-ray Raman scattering into excited valence electronic states. According to Ref. [1], dispersion effects are accessible due to momentum conservation [3]. Carlisle *et al.* [1] use the core hole to select states of p symmetry, but they neglect electronic and vibronic effects of the core hole in the intermediate state. The purpose of this Comment is to show that these effects should have measurable consequences in RIXS of graphite.

RIXS and the related technique of resonant photoemission (RPES) involve core excitations in the intermediate state. RIXS intensity variations roughly follow those of the x-ray absorption (XAS) spectrum, making the understanding of the XAS essential to understanding RIXS. Near-edge XAS of graphite is not well described by the C p density of states, since strong core hole effects influence both the location and shape of the peaks [4–6], but is reproduced by the calculated density of states on a $Z + 1$ atom (N) [4,6].

The first-principles theoretical [6] electronic width of the π^* resonance is only about 60% of the measured [5] value, which indicates that lattice relaxation plays an important role in XAS, and thus RIXS of graphite. A clear example of such vibrational effects is the $1s$ absorption of the nitrogen molecule, N_2 , which is interesting because of the formal equivalence of the two atoms. A $Z + 1$ description works well for the XAS spectrum [7]. The electronically narrow π^* peak is approximately 1.2 eV wide because of vibrational effects. In RPES, exciting to different vibrational states in the same intermediate electronic state give different vibrational final states [8]. In this case electronic dispersion is absent, but the RPES peaks show large shifts as a function of excitation energy. This suggests one *possible* role for relaxation in RIXS of graphite in explaining some of the shifts observed [1].

An important subtlety in graphite RIXS is the unexpectedly large intensity involving the π bands on excitation to the π^* edge region. Such emission should be forbidden in the simplest approximation, and requires a breaking of the atomic equivalence within the graphene unit cell in model calculations [1], suggesting strong coupling to symmetry-lowering vibrations [9]. This need not completely dephase the intermediate state if there is strong coupling to one or only a few modes, as observed for RIXS of benzene at its π^* resonance [10].

A RIXS calculation which follows the XAS intensity variations does not assure the correct result, however, because electronic and nuclear relaxation of the intermediate state continue during the life of the core hole. This

reduces dependence on excitation energy, because information on energy, momentum, and symmetry is lost in the electronic and vibrational continua. This simplifies the understanding of the RIXS process and points to conditions *when it will be applicable* via the role of perturbations on the (localized) intermediate state by its environment. An extreme example of the loss of structural information is the atomic Auger lines seen in O_2 after excitation to a dissociating state [11]. The role of electronic localization in RIXS is seen, e.g., in RPES of C_{60} [12]. The decay of the intermediate state by hopping of the pumped electron before the annihilation of the core hole was probed quantitatively, and related to a hopping matrix element which for the present considerations is more easily appreciated as a scattering term. Thus, though it is vibrations which can break the symmetry of the intermediate excited state in RIXS, it is the excitonic localization of the π^* levels [4–6] which promotes the resonant transitions.

More generally, this rules out RIXS involving the broad bands of metals, as opposed to semiconductors and semimetals, or narrow-banded materials, because of better screening of the core hole [6], which prevents the excitonlike effect necessary for resonance. Similar arguments indicate that RIXS will be much weaker if not absent in most cases for excitation much above the absorption edge. Thus a calculation of the $Z + 1$ impurity electronic structure would give valuable insight into the feasibility of measuring RIXS for an untested system.

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