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Reply to "Comment on 'Resonant inelastic x-ray scattering of MnO: $L_{2,3}$ edge measurements and assessment of their interpretation' "

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In their Comment to our recent paper [Phys. Rev. B **73**, 035111 (2006)], Müller and Hüfner proposed a comparison of our Mn $L_{2,3}$ resonant inelastic x-ray scattering (RIXS) data with low-energy electron energy-loss spectroscopy (EELS) measurements. The differences in the experimental spectra highlighted by the authors can be easily ascribed to the different cross sections in the two techniques, even when they probe the same subset of excited states, namely, the *dd* excitations. One important difference is that EELS is limited to quartet final states only, whereas RIXS can lead to doublets, too. Thus our theoretical interpretation of the RIXS spectra, made within two different models, is compatible with the traditional crystal-field analysis of EELS. As the Sugano-Tanabe diagram usually do not include the 3*d* spin-orbit and the interatomic superexchange interactions, their accuracy is limited to hundreds of meV and they should be utilized only for rough assignments of the spectral features. On the contrary, by calculating the RIXS spectral shape we could address more sophisticated models with remarkable agreement to the experimental results. This is hardly possible in the case of low-energy EELS, for which reliable simulations of the spectra are much more difficult.

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The Comment by Müller and Hüfner (MH) (Ref. 1) addresses the problem of comparing the spectral functions of MnO obtained by Mn L_3 resonant inelastic x-ray scattering (RIXS) and by low-energy electron energy-loss spectroscopy (EELS) in backscattering geometry. This issue was obviously not among the purposes of our original paper.[2] In fact we highlighted there that MnO RIXS data at high resolution are characterized by a very rich set of spectral features; those features can be interpreted at a high degree of accuracy as crystal-field excitations (*dd* excitations), and two different models were used to reproduce the experimental data, namely, the atomic crystal-field model (CFM) and the single impurity Anderson model (SIAM). The detailed comparison between different spectroscopies on the same compound is certainly an interesting problem and much will be learned from future work of this kind. However, in our opinion, the Comment does not add information to the available literature because the EELS measurements and their rough interpretation based on CFM are very close to those by Fromme *et al.*,[3] and the discussion of the apparent discrepancies between RIXS and EELS is largely questionable and uninformative. We do not agree with most of the objections reported in the Comment and we briefly reply here to those criticisms, both on the experimental and on the theoretical aspects of our original article.

In our paper,[2] in the work of Fromme[3] and, as a consequence, in the Comment,[1] the experimental data are interpreted within a model based on a single ion with crystal field. Obviously this picture is a simplified one because it treats the Mn 3*d* states as narrow and completely localized ionic levels. Nevertheless the simple CFM approach works remarkably well for a general assignment of the spectral features as *dd* excitations, both in RIXS and EELS. This demonstrates that the differences in the experimental results are not due to any intrinsic limitations of either RIXS or EELS but are rather due to *inherent probing differences in the two processes*. The fact that the CFM parameters derived from RIXS and EELS do not differ more than the spread of the parameters in the literature is, in our opinion, *an encouraging agreement in consideration of the simplification of the model.* Nevertheless, only in RIXS the actual spectral shape has been calculated (by us), whereas MH stated that "a calculation of intensities in EELS spectra of *d*-metal compounds is not very promising." This difference is, in our opinion, a strong point in favor of RIXS, together with its lower surface sensitivity, with the possibility of measuring in the presence of magnetic or electric fields and with the chemical selectivity provided by the resonance.

MH stated that EELS appear to be in contradiction to our RIXS results. In our opinion the different spectral shapes are not mutually contradictory because *RIXS and EELS are different processes* governed by different selection rules. RIXS is a second-order resonant process while the leading term in EELS is first order. The most fundamental difference, though, is in the angular momentum carried by the scattering particle: in RIXS the photon carries an angular momentum of 1 and in EELS the electron carried angular momentum of 1/2. The selection rules are thus different. In the $3d^5$ configuration with cubic crystal field, if we neglect the spin-orbit and the interatomic superexchange interactions, the ground state is the ${}^6A_{1g}$ term (high-spin ground state for $10Dq < 3$ eV);[4] the excited states are either quartets or doublets, differing thus from the ground state by 1 or 2 angular momentum units. In RIXS both quartets and doublets are thus reachable, whereas in EELS only quartets are allowed. Thus there is no reason to expect the spectral functions to be identical. Apparently on this point the Comment is self-contradictory because we can read that "there are (surprisingly) deviations (of EELS) with respect to the RIXS data" and, two lines lower, that "it is not obvious that (RIXS)results must agree with those of optical or EELS experiments (which may be called first-order techniques)." In our opinion there is nothing surprising: since the two methods probe the sample differently, a direct comparison between the RIXS and EELS features, as made in Table I of the Comment, is not really meaningful. Moreover, this approach is somewhat arbitrary because RIXS spectra are strongly dependent on the excitation energy across the resonance. Some RIXS features are well seen only at certain energies so that it is not clear how to select the features to be compared with EELS. This dependence on the incident photon energy is typical of the resonant nature of the process. We can consider it to be an advantage of the method as it makes it highly selective and thus easier to simulate theoretically. It is noteworthy that we are able to reproduce rather well this photon energy and polarization dependence with relatively simple models. This is why we believe that RIXS is sufficiently mature to study also complex systems.

The Sugano-Tanabe diagram shown by MH in Fig. 1 of the Comment is misleading: the actual $3d^5$ multiplet is much richer than reported in the figure, as it would appear more evidently if the $3d$ spin-orbit interaction and the interatomic superexchange interaction were added in the calculation of the dd excitations. An example for the (simpler) case of Ni^{2+} in NiO can be found in Ref. 5: once those interactions are taken into account each state is split into many contributions separated by tens of meV. As their cross sections in RIXS and EELS are different it becomes impossible to use the rough diagram of Fig. 1 of the Comment to accurately assign the peak positions: each spectral feature, in RIXS as well as in EELS, is often originated from a number of final states, even in the "simple" CFM. If one wants to assign the spectral features with accuracy better than 100 meV full calculations including the transition cross sections are then needed. As the $3d^5$ case is much more complicated than the $3d^8$, in Fig. 1 we make the comparison of two of our RIXS spectra with the Sugano-Tanabe diagrams presenting separately the quartets and the doublets. We have used the same values for the Slater integrals as in our original paper (i.e., 75% of the value calculated by Cowan's code[6]): $F^2=7.77$ eV and $F^4=4.82$ eV, corresponding to the Racah parameters[7] $B=837\ \mathrm{cm}^{-1}$ and $C=3087\ \mathrm{cm}^{-1}$. We highlight here that these values are much closer to those suggested by MH than usually thought: our B and C are 97% and 91% of those indicated in the Comment as being the "exact" ones. A better tuning of the Slater integrals (Racah parameters) together with the $10Dq$ crystal-field strength is probably possible using higher quality RIXS spectra, but our final choice is neither arbitrary nor unreasonable. Moreover, the values determined from EELS in Fig. 1 of the Comment are not definitive nor perfect: as MH declared at least two possible states present around 5.5–6.0 eV in their Sugano-Tanabe diagram have no correspondence in the EELS spectrum. A final remark on our Fig. 1: quartet final states seem to have stronger intensity in RIXS in general, but when exciting at L_2 [spectrum (G)] it seems that doublets gain in intensity.

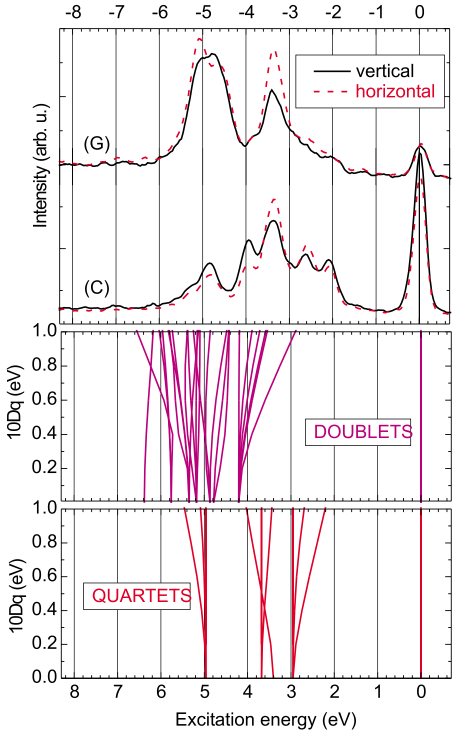

FIG. 1. (Color online) Comparing the Sugano-Tanabe diagram for $3d^5$ configuration to the experimental RIXS spectra measured at two excitation energies (c) at L_3 and (g) at L_2. Top panel, RIXS spectra: black solid (red dashed) lines for linear polarization perpendicular (parallel) to the scattering plane; same spectra presented in Fig. 1 of Ref. 2. Middle and bottom panels: Sugano-Tanabe diagrams. We have rescaled the Slater integrals to 75% of the value calculated by Cowan's code (Ref. 6), as in our original calculations with CFM. We separate here the quartet from the doublet final states to highlight that RIXS can reach both types of final states and that at L_2 doublets seem to be more intense than quartets.

In Fig. 2 (bottom panel) we summarize the comparison between MH's ($F^2=8.19$ eV, $F^4=5.32$ eV, and $10Dq=1.3$ eV) and our parameters (7.77, 4.82, and 1.0 eV, respectively). In the top panel of the same figure we present the full set of states calculated by introducing the $3d$ spin-orbit and 5 meV effective superexchange interactions. In this case the above classification in doublets and quartets is no more strictly valid because the total spin and total orbital momenta are not good quantum numbers anymore. This implies that the above arguments on selection rules in RIXS and EELS are not rigorous although they remain a good approximation. Thus a full calculation of the scattering cross sections has to be made in order to enter into more detailed discussions about the crystal-field parameters.

Another objection concerns our choice of rescaling the Slater integrals with respect to the values calculated with Cowan's program[6] or optimized on atomic spectroscopy data. MH stated that "the perturbation by the solid should be approximated by just one parameter, namely, the CF

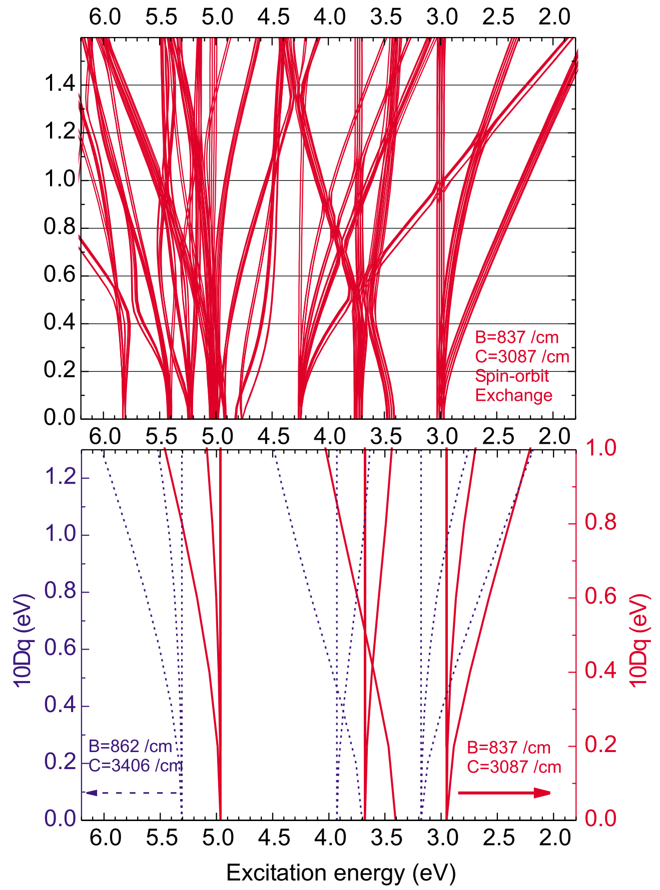

FIG. 2. (Color online) Comparing the Sugano-Tanabe diagrams for $3d^5$ configuration obtained with our Slater integrals to those suggested by MH. In the bottom panel we show the energy diagrams of quartet states only: for our parameters up to $10Dq = 1.0$ eV (red solid lines, right-hand scale), for MH's parameters up to $10Dq = 1.3$ eV (dashed blue lines, left-hand scale). We notice that some energy can be obtained by either parameter combinations. In the top panel the full multiplet is presented having included the $3d$ spin-orbit interaction and the interatomic superexchange interaction. The states have there mixed character and they cannot be separated into doublets and quartets anymore.

parameter $10Dq$, while the atomic part of the Hamiltonian can still be described by the Racah parameters (the counterparts of the Slater integrals) of the free Mn^{2+} ion." We cannot understand on what basis this statement is derived. It is well known that the perturbation by the solid should modify both $10Dq$ and Slater integrals (or Racah parameters) of the free Mn^{2+} ion. By the hybridization effect, the Mn $3d$ wave function mixes with the O $2p$ wave function so that the $3d$ weight is reduced in the Mn site and the Slater integrals (multiplet coupling strength) should be reduced (see, for instance, paragraph 5.3.2.1 of Ref. 8). Of course, there is some ambiguity in the choice of modification parameters for $10Dq$ and Slater integrals, which are correlated with each other so that we would find a different $10Dq$ by using another rescaling parameter for Slater integrals. In order to minimize this ambiguity, it is necessary to check that the result of the CFM calculations with two parameters can well reproduce, as a reasonable approximation scheme, the result of SIAM calculations. This is just what we have done in our paper. If MH claimed that the perturbation by the solid should be approximated by just one parameter, they should demonstrate that this conclusion can be derived reasonably from a more basic model, such as SIAM, which includes explicitly both solid-state hybridization and atomic multiplet effects.

If we understand correctly, MH said that our treatment of RIXS is (over)simplified and that a more appropriate theory is found in Platzman and Isaacs.[9] In our opinion the two treatments are actually equivalent. Our theory is based on the Kramers-Heisenberg formula [Eq. (5) of Ref. 10], which is exactly Platzman and Isaacs's Eq. (1) (Ref. 9) when considered at resonance, as explained by them.

Finally MH found that too many parameters were used in SIAM calculations. These are state of the art model calculations and as such they contain free parameters. However there is much less freedom in the choice of the parameters than one might imagine at first sight, once one keeps the consistency with the fitting of other spectroscopies, where some parameters such as U_{dd} are more directly accessed. In the future it will be certainly possible to reduce the number of parameters, thanks to the progress of first principle calculations. Finally we notice here again that the meaning of $10Dq$ in SIAM is different than in CFM because in SIAM the mixing of Mn $3d$ with O $2p$ states is explicitly taken into account via the hybridization strength parameters $V(e_g)$ and $V(t_{2g})$. The dd excitations are most directly influenced by V's, R_c, R_v and, obviously, $10Dq_{\mathrm{SIAM}}$. Their optimization was made also by considering the absorption spectra.

To conclude we notice that the proposed comparison of RIXS and low-energy EELS is not well suited due to unavoidable experimental drawbacks. The main difficulty comes from the lack of information, at present, on the momentum transferred to the electronic dd excitations in the two scattering processes. In fact we expect some dependence of the peak energy positions on the transferred momentum although MnO is not bandlike in the traditional sense. In this connection the coupling of dd excitations to the lattice and magnetic degrees of freedom could have an effect. To recover that information the RIXS measurements should be made at various scattering angles and/or sample orientations. Moreover, electron energy loss should be studied with high energy electrons in transmission with control of the transferred momentum as done in transmission electron microscopes.[11] On the contrary, in backscattering low energy EELS the transferred momentum to the dd excitation is hardly accessible due to large-angle elastic-scattering processes, which makes the determination from the raw data of the actual transferred momentum a serious problem in itself.[12] Moreover the undeniable surface sensitivity of low-energy EELS further complicates things: although MH suggested that only the scattering cross sections and not the energies are modified at the surface, the EELS spectra could anyway be heavily altered and specific experimental investigations should be made before leading to sharp conclusions.

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