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

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Recently, Ghiringhelli *et al.* [Phys. Rev. B **73**, 035111 (2006)] reported on the *d-d* crystal field and charge-transfer excitations in MnO by using resonant inelastic x-ray scattering (RIXS). The data were analyzed with the single impurity Anderson model (SIAM) as well as with the crystal-field model (CFM), with both models providing very different parameters. The results of their CFM analysis are in conflict with the results obtained by analyzing electron-energy-loss spectroscopy (EELS) data with the same model.

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Transition-metal compounds have been a subject of solid-state research for a long time due to their many interesting properties. The most important one is perhaps the occurrence of what is now often called Mott insulation.[1,2] This means insulating behavior in a system with partially filled bands (such a system would be metallic in simple band theory) due to large on-site Coulomb interactions. The gap in these systems is often called a Mott gap, though matter can be more complicated. The occurrence of superconductivity in the cuprates and of very large magnetoresistance in the manganites has increased the interest in this class of compounds.[2]

The low energy electronic excitations in these systems are important for the understanding of their properties. They have been investigated by optical spectroscopy, electron-energy-loss spectroscopy (EELS) and by resonant as well as nonresonant inelastic x-ray scattering (RIXS, NIXS).

In a recent paper, Ghiringhelli *et al.*[3] presented RIXS experiments on MnO, a simple prototype transition-metal compound, measuring the *d-d* crystal field and charge-transfer excitations. If a new method is used to investigate an established system and the data are analyzed in a known framework, two points have to be addressed: What additional information does the new method provide, and what kind of new information does the new analysis yield? In light of this, we would like to comment on the paper by Ghiringhelli *et al.*[3] as follows:

The RIXS technique is by no means as trivial as the authors make it look. A detailed discussion of the problems has, e.g., been given by Platzman and Isaacs.[4] The discussion of Ghiringhelli *et al.*[3] uses Eq. (5) of the work of Kotani and Shin[5] which contains considerable simplifications. In order to document the experimental situation, the RIXS data by Ghiringhelli *et al.*[3] (taken from 4 spectra of this work) are compared to the EELS data of Fromme *et al.*[6] and the EELS data of the present work in Table I. While there is (not unexpectedly) a good agreement between the two sets of EELS data, there are (surprisingly) deviations with respect to the RIXS data. This is probably due to the fact that the second-order RIXS process is a quite complicated one,[4] where it is not obvious that its results must agree with those of optical or EELS experiments (which may be called first-order techniques). This problem is not addressed by Ghiringhelli *et al.* in Ref. 3.

The second point concerns the data analysis given by Ghiringhelli *et al.*[3] Their data have been analyzed by the single impurity Anderson model (SIAM) and the crystal-field model (CFM). Although the quality of the fits using the two models is similar, they state "For MnO we find that the CFM to SIAM renormalization factor is 1/2. It must be noted that the SIAM value ($10\mathrm{Dq}_{\mathrm{SIAM}}=0.5$ eV) if used in CFM would produce a completely wrong RIXS spectrum. …Finally we note that both SIAM and CFM parameters are different from those obtained with a cluster model…."[3] These considerable discrepancies are not further addressed, and within this context, we cannot agree with the authors, that "…the results on MnO presented here have a double impact. On MnO itself, because we can determine very accurately the value of important theoretical parameters…."[3] To the contrary: The parameters obtained from the RIXS data span the same wide range as the values reported in literature (e.g., from $10\mathrm{Dq}=0.7$ eV in Ref. 7 to $10\mathrm{Dq}=1.35$ eV in Ref. 8), and they are therefore far from being accurately determined. We also note that in the SIAM analysis Ghiringhelli *et al.*[3] use at least nine parameters, compared to one parameter in our analysis (see below).

To be more specific: Within the analysis of the RIXS data[3] by the CFM, the *d-d* excitations were approximated by using a CF parameter 10Dq, that "is about 25%–35% smaller than the values reported in the literature."[3] Additionally, the Slater integrals have been also rescaled to 75%. At this stage, we do not intend to argue about the "exact" value of the CF parameter 10Dq, but instead, we would like to refer to the rescaling of the Slater integrals.

To our knowledge, MnO represents the prototype system for an analysis of the *d-d* excitations within the CFM, which meets the most simple ansatz: The perturbation by the solid should be approximated by just one parameter, namely the CF 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 want to demonstrate this by showing a CFM analysis of an EEL spectrum (this work) on MnO in Fig. 1. The experimental loss energies for the *d-d* excitations are compared to the energy levels of a Tanabe-Sugano diagram.[9] In our analysis, the Racah parameters were fixed at those values

TABLE I. Comparison of *d*-*d* excitation energies (in eV) by RIXS (taken from Ref. 3) and EELS (taken from Ref. 6 and this work). The assignment of the crystal-field transitions in the last column is based on the results from Fig. 1.

RIXS spectrum C pol. par.	RIXS spectrum C pol. perp.	RIXS spectrum E pol. par.	RIXS spectrum E pol. perp.	(CSP) EELS	EELS	CF transition $^6A_{1g}(^6S)\rightarrow$
1.65	1.60	1.55	1.50			
2.20	2.20	2.20	2.25	2.13	2.16	$^4T_{1g}(^4G)$
				2.40[a]		
2.75	2.80	2.75	2.75	2.82	2.86	$^4T_{2g}(^4G)$
	3.20[b]	3.15[b]	3.10[b]			
				3.31[c]	3.25[c]	$^4E_g(^4G), {}^4A_{2g}(^4G)$
3.55	3.55	3.50			3.50	$^4T_{2g}(^4D)$
		3.65[b]	3.65[b]			
				3.82[c]	3.83[c]	$^4E_g(^4D)$
4.15[b]	4.15[b]	4.10[b]	4.10[b]			
				4.57[c]	4.63[c]	$^4T_{1g}(^4P)$
5.10	5.10	5.05	5.05	5.08	5.13	$^4A_{2g}(^4F)$
5.55	5.55	5.45	5.45	5.38[a]		$^4T_{1g}(^4F)$
6.00			6.00			$(^4T_{2g}(^4F))$
	6.20	6.20				
Ref. 3	Ref. 3	Ref. 3	Ref. 3	Ref. 6	This work	This work

[a] Weak.

[b] No counterpart in the EELS data.

[c] No counterpart in the RIXS data.

that fit the energies of the free Mn^{2+} ion (full squares in the lower part of Fig. 1)[10] as well as the energies of the non-Dq dependent excitations of the EELS spectrum. The CF parameter 10Dq was then varied to that value, which fits the remaining energy losses (yielding $10\mathrm{Dq}=10\,700/\mathrm{cm}=1.3$ eV). From Fig. 1, it is evident that it is possible to reproduce both the energies of the free Mn^{2+} ion as well as the energies within the CF of the solid by the same set of Racah parameters; i.e., there is no need to rescale these parameters. In other words, for MnO, the transition from the free Mn^{2+} ion to Mn^{2+} within the solid takes place just by applying a proper CF described by one parameter, namely the CF parameter 10Dq. Ghiringhelli *et al.*[3] probably get in their CFM analysis $10\mathrm{Dq}=1.0$ eV because they rescale the Slater integrals to 75%, with no reasons given. (Adjusting these parameters in our work would of course improve the fit—which an addition of free parameters always does—but such an improvement would come at the cost of giving up the simple transparent model. We did not make any attempt to reproduce the intensities within the EELS spectrum: In contrast to RIXS, EELS represents a very surface sensitive technique, and therefore, surface states can contribute to the spectrum. Recent quantum chemical *ab initio* calculations have shown that the surface states of MnO differ however from the bulk states only by a few meV.[11] As a consequence, contributions from surface states have an impact on the intensity distributions within a spectrum, while the energy scale is hardly affected by the presence of surface states. But even without those surface state contributions, the determination of intensity distributions within an EELS spectrum is a difficult task, even if the scattering mechanism is described

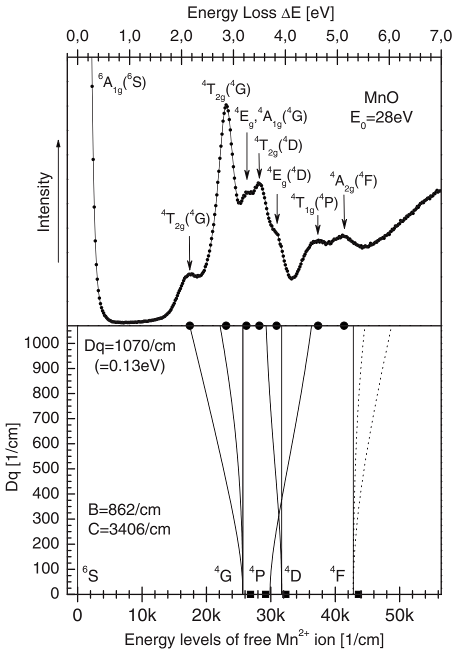

FIG. 1. EEL spectrum of MnO/Ag(001), taken along the (110) axis in off-specular scattering geometry at a primary energy $E_0=28$ eV (FWHM 250 meV), compared to the Tanabe-Sugano diagram for the $3d^5$ configuration of Mn^{2+}, calculated from the matrices listed in Ref. 9. Black dots: energy losses of the EEL spectrum on MnO; black squares: energies of the ^{2S+1}L multiplets of the free Mn^{2+} ion (i.e., center of gravity of the $^{2S+1}L_{|L+S|\ldots|L-S|}$ levels from Ref. 10). The $^4T_{1g}(^4F)$ and $^4T_{2g}(^4F)$ terms (dotted lines) were not observed in the EELS data.

in a more sophisticated way. The investigation of *d*-*d* exchange scattering cross sections within an *R*-matrix approach, as performed for NiO by Jones *et al.*,[12] has shown that the angular intensity distribution of a single transition can be described very well, cf. Figs. 13 and 14 in Ref. 12 and Fig. 6 in Ref. 13. But on the other hand, if the cross sections are calculated for a whole spectrum at a fixed scattering geometry, the calculated intensity distributions deviate strongly from the experimental data, cf. Figs. 13 and 14 in Ref. 12. These reasons taken together suggest that a calculation of intensities in EELS spectra of *d*-metal compounds is not very promising).

We emphasize that apart from the differences, which are caused by applying the same model in a different way, both techniques also provide different raw data. The energies for the *d*-*d* excitations in the RIXS spectra by Ghiringhelli *et al.*[3] are different from the energies observed in EELS. From Table I, one notices that RIXS provides signals at 3.15 and 4.15 eV, for which there are no counterparts in the EELS data (and no signals are expected from the Tanabe-Sugano diagram). On the other hand, the EELS signal at 3.30 eV is not observed in the RIXS experiment. These differences must be related to some fundamental differences in the excitation mechanism of both techniques (Note that apart from the enhanced resolution, the EELS data in Fig. 1 exactly match the EELS data in Ref. 6, both recorded on different samples and different setups).

For both techniques, the transition probabilities are determined by a variety of different factors. As an illustrative example, one can point to the different spins of the probing particles, representing just one of these factors. EELS and RIXS are similar (especially with respect to the spin forbidden excitations on MnO) that both excitation mechanisms include a coupling between the spins of the primary/scattered probes and the angular momenta of the target. Due to the different spins of the probing particles, the transition probabilities of the various scattering channels are weighted by different Clebsch-Gordan coefficients, cf. Ref. 14.

The comparison of RIXS and EELS data shows that both techniques provide different results, even for a simple 3*d* TM prototype system like MnO. Before turning to more complex systems, as suggested in Ref. 3, it would be an interesting task to elaborate the details of both excitation mechanisms in order to attribute the different experimental results to the differences of both techniques, at least for simple model systems. At this stage, it is therefore doubtful whether "…the results on MnO presented here have a double impact …for RIXS as an advanced spectroscopic technique, because we assess the interpretation framework useful to future experiments on more complex 3*d* TM systems."[3] As long as different techniques describe the same system in a different way, even when analyzing the data within the same model, the investigation of more complex systems remains a difficult task—for RIXS to the same degree as for other spectroscopic techniques.

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[14] If the spins of the primary/scattered particles are described by $|j_1,m_1\rangle$ and $|j_3,m_3\rangle$, respectively (with $j_1,j_3=1/2$ for EELS, $j_1,j_3=1$ for RIXS), while the total angular momenta of the initial/final states of the target are described by $|j_2,m_2\rangle$ and $|j_4,m_4\rangle$, respectively, then the amplitude of the transition probability via an intermediate state $|J,M\rangle$ is given by

$$\omega_{12\rightarrow 34}\propto\left(\begin{array}{cc|c} j_1 & j_2 & J\\ m_1 & m_2 & M\end{array}\right)\cdot\left(\begin{array}{cc|c} j_3 & j_4 & J\\ m_3 & m_4 & M\end{array}\right),$$

with the bracket terms describing Clebsch-Gordan coefficients. If a peak is formed by contributions of final states with different j_4, then, both techniques may provide different excitation energies (as given by the center of gravity of the contributing j_4 states) due to the different weight of each j_4 contribution.