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LETTER TO THE EDITOR

Spin and symmetry in low-energy electron energy-loss spectroscopy of transition metal oxidesJ J M Michiels[†], J E Inglesfield[‡], C J Noble[§], V M Burke[§] and P G Burke^{||}[†] Max-Planck-Institut für Festkörperforschung, Heisenbergstrasse 1, D-70569 Stuttgart, Germany[‡] Department of Physics and Astronomy, University of Wales Cardiff, PO Box 913, Cardiff CF2 3YB, UK[§] CCLRC Daresbury Laboratory, Daresbury, Warrington WA4 4AD, UK^{||} Department of Applied Mathematics and Theoretical Physics, Queen's University, Belfast BT7 1NN, UK

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Abstract. The ratio of spin-flip to non-flip intensity in low-energy electron energy-loss spectroscopy for multiplicity-changing transitions within the 3d multiplet in NiO and CoO can be found exactly. It is shown to be independent of scattering geometry, incident energy and multiple scattering if well-defined local spins are assumed. For non-multiplicity-changing transitions this ratio can be calculated approximately, using *R*-matrix techniques. The angular dependence of the scattering processes at low kinetic energies of the incident electron can be understood in terms of the point group symmetry at the target ion and the contribution of dominant angular momentum components to incoming and outgoing electron waves.

Electron energy-loss experiments provide a detailed probe of the electronic structure of solids, and in this letter we discuss the interpretation of low-energy EELS (LE-EELS) experiments on transition metal oxides. When the electron beam energy is much greater than the excitation energy, dipole scattering dominates and a description in terms of the Born approximation for both direct and exchange scattering can be used. However, this description is no longer valid at incident electron energies of less than 100 eV (say), where multiplet effects are apparent in the spectrum. In our work we study low-energy electron scattering from oxides, using a local description of scattering from the transition metal ion treated as a many-body system.

Recent experiments on NiO using polarized low-energy electron beams [1, 2], and earlier spin-averaged experiments [3, 4], show a substantial degree of dependence on the incident electron energy, including resonance effects, and a dependence on the type of excitation being studied (bulk versus surface, and excitations to states with different spin multiplicity or cubic symmetry index). In a Born treatment of dipole scattering from an atom [5], both direct and exchange amplitudes (*f* and *g* respectively) fall off with increasing scattering angle, *f* falling off much more rapidly. In non-dipole scattering from transitions within the d multiplet, there is much more complicated angle dependence, which depends on the particular transition.

As dipole and spin-selection rules are no longer valid, in this letter we shall look for new symmetry rules by considering the angular behaviour of spin-flip and non-flip differential scattering cross sections for excitations within the 3d multiplet. We will see that a classification is possible on the basis of the point group symmetry and spin of the

final state of the transition metal ion (Ni^{2+} and Co^{2+}). This is a generalization of the work by Goddard *et al* who have studied selection rules in electron-impact spectroscopy for free atoms (and molecules) [6].

Our theoretical description of the loss processes in low-energy EELS is based on a generalization of R -matrix theory [7–9] to solid-state systems. The central idea in R -matrix theory is to separate space into an inner region, where the scattering electron fully interacts with the target ion (for example Ni^{2+}), and an outside region, where the electron moves in an effective field. To generalize to solid-state systems like NiO we include the effects of hybridization of oxygen ligands with the 3d orbitals on the central Ni^{2+} ion. This is done in an effective way by applying a parametrized crystal-field potential and a scaled Coulomb potential (factor 0.7 [9–11]) in the inner region. The form of the crystal-field potential in terms of spherical harmonics Y_{lm_l} is

$$V_c(r, \theta, \phi) = \beta r^4 \left[Y_{40} + \left(\frac{5}{14} \right)^{1/2} (Y_{44} + Y_{4-4}) \right] + V_M. \quad (1)$$

β is fitted (graphically) in an N -electron target calculation to reproduce the electron energy losses in LE-EELS, and V_M is a constant energy shift due to the Madelung potential, fitted to Hartree–Fock band-structure calculations [12]. Our values for β and V_M are 0.0418 Hartree and 0.75 Hartree respectively.

In the cubic representation the expression for the differential scattering cross section (see also [13]) can be written as follows:

$$\begin{aligned} \frac{\partial \sigma(\mathbf{p}'i'm' \leftarrow \mathbf{p}im)}{\partial \Omega} &= \frac{(2\pi)^2}{p^2} \frac{1}{n_\alpha} \sum_{P S M_p} \sum_{P' S' M'_p} \sum_{\substack{p_2 h l \\ p_2' h' l'}} \sum_{\substack{p_2'' h'' l'' \\ p_2''' h''' l'''}} \langle \tilde{\phi}_{i'(p'_i)p_2'h'l'}^\Gamma | T | \tilde{\phi}_{i(p_i)p_2 h l}^\Gamma \rangle \\ &\times \langle \tilde{\phi}_{i'(p'_i)p_2''h''l''}^{\Gamma'} | T | \tilde{\phi}_{i(p_i)p_2'h'l'}^{\Gamma'} \rangle^* \sum_{M_S M'_S} \sum_{M_S M'_S} \left(S M_S \left| S_i M_{S_i} \frac{1}{2} m \right. \right) \\ &\times \left(S' M'_S \left| S_i M_{S_i} \frac{1}{2} m \right. \right) \left(S M_S \left| S'_i M'_{S_i} \frac{1}{2} m' \right. \right) \left(S' M'_S \left| S'_i M'_{S_i} \frac{1}{2} m' \right. \right) \\ &\times \left\{ \begin{array}{c} p_2 h l \\ p_2'' h'' l'' \\ P M_P P' M'_P \end{array} \right\}_p \left\{ \begin{array}{c} p_2' h' l' \\ p_2''' h''' l''' \\ P M_P P' M'_P \end{array} \right\}_{p'} \quad \text{where } \Gamma \equiv \{P S \pi\} \end{aligned} \quad (2)$$

and where $(S M_S | S_i M_{S_i} \frac{1}{2} m)$ is a Wigner coefficient. Here p is the magnitude of the momentum \mathbf{p} of the incident electron. P, p_1 , and p_2 indicate the cubic symmetries of respectively the compound state (target + electron) with spin S and spin component M_S , the target i with spin S_i and spin component M_{S_i} , and the scattering electron with spin component m and angular momentum l ; h indicates that different cubic symmetries p_2 can be associated with each l . n_α gives the degeneracy of the incoming channel and is equal to $2S_i + 1$, assuming a completely polarized beam of incoming electrons. The brackets in this equation have the following meaning:

$$\begin{aligned} \left\{ \begin{array}{c} p_2 h l \\ p_2'' h'' l'' \\ P M_P P' M'_P \end{array} \right\}_p &= \sum_{\mu_2, \mu_2''} \left(\sum_{m_1} b_{h l m_1}^{* p_2 \mu_2} Y_{l m_1}(\hat{p}) \right) \left(\sum_{\mu_1} (P M_P | p_1 \mu_1 p_2 \mu_2) (P' M'_P | p_1 \mu_1 p_2'' \mu_2'') \right) \\ &\times \left(\sum_{m_1''} b_{h'' l'' m_1''}^{p_2'' \mu_2''} Y_{l'' m_1''}(\hat{p}) \right). \end{aligned} \quad (3)$$

This bracket depends on the angle of the incoming electron beam \hat{p} , with momentum \mathbf{p} , and contains the coefficients $b_{h l m_1}^{p_2 \mu_2}$ which transform (Condon–Shortley) spherical harmonics

Y_{lm_l} into real cubic harmonics, and cubic Clebsch–Gordan coefficients ($PM_P|p_1\mu_1p_2\mu_2$). M_P , μ_1 , and μ_2 are the basis function indices for the cubic symmetries P , p_1 , and p_2 respectively. The scattering properties of the target are contained in the T -matrix elements $\langle\tilde{\phi}_{i'(p'_1)p'_2h'l'}^\Gamma|T|\tilde{\phi}_{i(p_1)p_2hl}^\Gamma\rangle$ that describe the scattering from channel $|\tilde{\phi}_{i(p_1)p_2hl}^\Gamma\rangle$ into channel $|\tilde{\phi}_{i'(p'_1)p'_2h'l'}^\Gamma\rangle$ [9]. The channels $\tilde{\phi}^\Gamma$ are symmetrized combinations of a target state and the spin and orbital part of the scattering electron wavefunction. In this evaluation of the differential cross section, we have averaged over the ionic spins, because NiO and CoO have a multi-domain structure [14, 15]. The spins are therefore effectively randomly oriented with respect to the spin-quantization axis of the incoming electrons even below the Néel temperature.

Just from the local point group symmetry and the properties of the Wigner coefficients [16], several general results can be derived. We begin by considering the spin-polarized differential cross sections of NiO, where the spin-flip to non-flip ratio of the cross section may be calculated. In equation (2) only certain combinations of Wigner coefficients are non-vanishing. Thus for the multiplicity-changing transitions from the triplet ground state with $S_i = 1$ to a singlet excited state with $S_{i'} = 0$, for the non-spin-flip transitions the only non-vanishing combination is $(\frac{1}{2}\frac{1}{2}|10\frac{1}{2}\frac{1}{2})^2(\frac{1}{2}\frac{1}{2}|00\frac{1}{2}\frac{1}{2})^2$ which equals $\frac{1}{3}$. Likewise for the spin-flip transitions the only non-vanishing combination is $(\frac{1}{2}-\frac{1}{2}|1-1\frac{1}{2}\frac{1}{2})^2(\frac{1}{2}-\frac{1}{2}|00\frac{1}{2}-\frac{1}{2})^2$ which equals $\frac{2}{3}$. This means that the spin-flip to non-flip ratio is 2. This conclusion is independent of the scattering geometry, and the local symmetry at the Ni^{2+} ion— O_h (bulk Ni^{2+} ion) or C_{4v} (surface Ni^{2+} ion). It remains valid for multiple elastic scattering by other ions in the outer region. It also remains valid for larger R -matrix inner regions (e.g. with a NiO_6^{10-} cluster instead of a Ni^{2+} ion), as long as the spin is well defined within the inner region. For CoO, which has a different electronic configuration (d^7 instead of d^8 in NiO), we arrive at an identical conclusion: here also the spin-flip to non-flip ratio for multiplicity-changing transitions is independent of the scattering geometry, local symmetry, and multiple scattering, and is again two. This remarkable conclusion holds only for the multiplicity-changing transitions; for triplet–triplet transitions in NiO and quartet–quartet transitions in CoO, the behaviour of the spin-flip to non-flip ratio is more complicated and has to be calculated explicitly.

In figure 1 we illustrate the contribution of spin-flip and non-flip scattering to particular loss transitions in LE-EELS from NiO(001), calculated using our R -matrix method. Here the incoming scattering angles (θ_i, ϕ_i) remain fixed at $\phi_i = 0$ and $\theta_i = 45^\circ$, where ϕ_i is measured with respect to the (100) axis and θ_i is the angle with respect to the surface normal. The orientation of the outgoing polar angle θ_f is then varied ($\phi_f = 180^\circ$) and the intensity of both the spin-flip and non-flip contributions is plotted. The results in figure 1(a) agree with the above statement that the spin-flip contribution to the multiplicity-changing transitions is double the non-spin-flip one. In the triplet–triplet transitions on the other hand the non-flip transitions are stronger (figure 1(b)) and the spin-flip to non-flip ratio changes with scattering angle. For example, in forward-scattering geometry the non-flip intensity is about two times the flip intensity, whereas at scattering angle = 125° it is eight times the flip intensity. It would be useful to measure the spin-flip to non-flip ratio for the triplet–singlet transitions, because deviations from 2 presumably come from non-locality of the Ni^{2+} spin. It may, however, be difficult to extract the exact ratios in experimental studies, due to backgrounds of surface states, defect states [1], and charge-transfer excitations across the surface and bulk band gap which show different scattering behaviour.

We now turn from arguments based on spin to the effects of spatial symmetry on LE-EELS spectra and consider those scattering events with incoming and outgoing electron

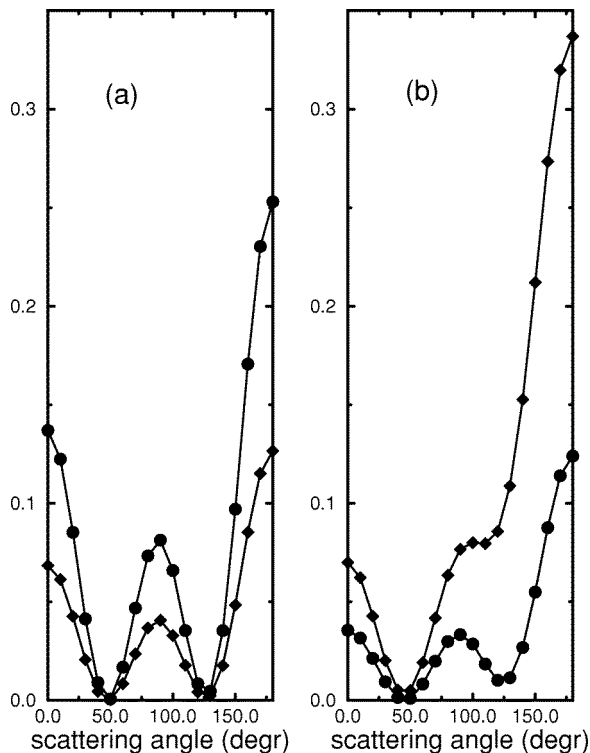


Figure 1. The spin-flip (circles) and non-flip (diamonds) differential cross sections for two transitions in NiO (a) ${}^3A_{2g} \rightarrow {}^1T_{1g}$ (3.28 eV energy loss) and (b) ${}^3A_{2g} \rightarrow {}^3T_{1g}$ (1.75 eV energy loss). The scattering angle is with respect to the forward-scattering direction and is related to the outgoing polar angle: $\theta_f = 135^\circ - \text{scattering angle}$. Note that $\theta_i = 45^\circ$, $\phi_i = 0^\circ$, and $\phi_f = 180^\circ$. The y-axis is in units of a_0^2 .

beams in one scattering plane. The symmetry elements of the point group define which scattering planes are equivalent and also determine the special geometries for which the cross sections must be zero. This latter type of ‘symmetry rule’ follows when the ingoing and outgoing electron beams are oriented in parallel fashion along a particular symmetry axis, or in a particular mirror plane. For example, at $\theta_i = 45^\circ$, $\phi_i = 0^\circ$, the excitations to the A_{1g} and T_{2g} multiplet states show zero intensity for backward and forward scattering, whereas the other excitations have finite probability in these geometries.

This follows from the transformation properties of the final states and the corresponding matrix elements. For example $\langle p'A_{1g}|T|pA_{2g}\rangle$ must be invariant under a twofold rotation along the direction of incidence. In this case the A_{2g} (ground) state changes sign under rotation, but the A_{1g} state is unaffected. If the momenta are both parallel to the symmetry axis this leads to a sign change of the matrix element, and consequently the matrix element must be zero for forward- and backward-scattering geometry. The other excitations have final states with different transformation properties and therefore do not necessarily show zero intensity under these conditions. Again the conclusions are not changed if a bigger cluster is used to describe the scattering process (for example NiO_6^{10-}) or if multiple-scattering effects are taken into account.

To illustrate this spatial symmetry rule, figure 2 shows the differential cross sections calculated from equation (2) as a function of scattering angle for a number of final states.

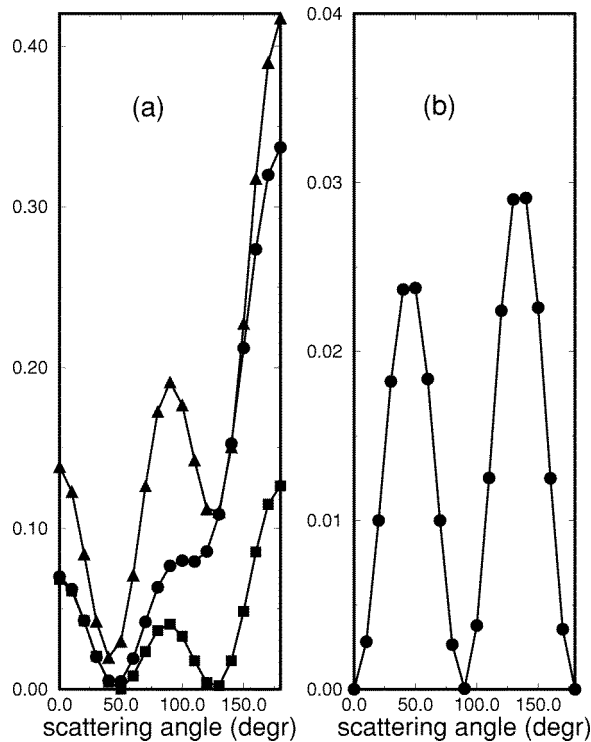


Figure 2. The non-flip differential cross sections for NiO corresponding to transitions from the ground state ${}^3A_{2g}$ to final states with symmetry ${}^1T_{1g}$ (a) and to a final state with symmetry ${}^1A_{1g}$ in (b). The loss energies in (a) are 3.28 eV (squares), 3.13 eV (triangles), and 1.75 eV (circles). The loss energy in (b) is 2.80 eV. The definition of the axes is the same as in figure 1.

The incoming electron beam is oriented along the $[101]$ axis, i.e. with $\theta_i = 45^\circ$, $\phi_i = 0^\circ$. It is clear from figure 2(a) that final states with the same symmetry (here T_{1g}) have cross sections which vary in a similar way. In this case the cross sections are clearly non-zero in forward- and backward-scattering geometries, with an angular behaviour dominated by $l = 2$ outgoing electron angular momentum. Figure 2(b) shows results for an A_{1g} final state, and the cross sections do indeed go to zero in forward- and backward-scattering geometries; once again the dominant contribution is due to $l = 2$. Thus the final-state symmetry determines the zeros in the cross section at certain symmetry-related angles.

For a more detailed description of the angle dependence, the contribution of each value of electron angular momentum to the T -matrix should be considered. The T -matrix elements coupling the incident electron angular momenta to l greater than 2 for the outgoing electrons are small, and this is compatible with the d-wave form of the scattering shown in figure 2. This is presumably a consequence of the negligible weight of larger values of angular momentum in wave packets corresponding to the 20 eV scattering electrons that we consider here. This means that very rapid angular variations in the differential cross section, when considering for example scattering geometries close to specular (see in particular figure 2(a) in [4]), cannot be explained in terms of our single-scattering description. This variation must be the result of additional multiple elastic scattering (before or after the inelastic collision with the Ni^{2+}), thus providing coupling to higher electron angular momenta. It would certainly be interesting to follow the angular variation more closely in experiments,

in particular orienting the incoming electron beam along a symmetry axis, and measuring the outgoing electron beam over a large range of polar angles in the same scattering plane. This could yield extra information about the final-state symmetry in various excitations, the contribution of different electron angular momentum components to the cross section, and the importance of multiple scattering.

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