Rydberg-Klein-Rees analysis.

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Line Shape of the $3p$ Excitation in the Electron Energy-Loss Spectrum of Nickel Metal

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The line shape of the electron energy-loss spectra due to $3p \rightarrow 3d$ excitation is reported for Ni. The observation is interpreted by a Fano-type interaction in which the excited configuration decays by Coster-Kronig processes into the continuum of excitations of the $3d$ band. These processes appear to hold generally for the transition metals in both electron scattering and soft-x-ray absorption.

The spectra of the transition metals Mn to Ni in the vicinity of the $3p$ core-level excitation (~60 eV) exhibit a highly asymmetric line shape, the origin of which has been a topic of conjecture.[1,2] These spectra have recently been studied both by optical absorption using a synchrotron light source,[1,3] and by electron energy-loss spectroscopy (ELS).[2,4] In the present paper we report detailed ELS measurements on the $3p$ line shape for Ni.

Compared with other transition metals, Ni presents a relatively simple case for interpretation because the $3p \rightarrow 3d$ excitation results mainly in the final-state configuration $3p^5 3d^{10}$. Thus it is not necessary to take account of the exchange interaction between the p and d holes which may split excited levels, in general a complicating factor.[5]

We interpret the ELS results in terms of the resonant interaction between an excitation to a discrete level and a continuum, and compute the spectral density from the general formalism for such interactions given by Fano.[6]

These considerations indicate that the excited electronic configuration consisting of a $3p$ hole and a $3d$ conduction electron interacts strongly with the continuum of configurations resulting from excitations from the $3d$ band. This configuration interaction, rather than the empty $3d$ state density, dominates the $3p$ line shape.

The electron energy-loss spectra were obtained with conventional four-grid low-energy-electron-diffraction (LEED) optics used as a retarding-potential analyzer. The experiment was done at normal incidence and all electrons emitted within 80° of the surface normal were collected. Both the energy distribution of scattered electrons $N(E)$ and its energy derivative $N'(E)$ were measured. Cathode modulation was used to suppress the "true-secondary" electron current and struc-

ture due to Auger electrons.[7] The energy resolution was slightly better than 1% of the primary energy E_p for $E_p > 100$ eV.

Single-crystal Ni(001) surfaces were prepared using standard techniques[8] and were maintained under ultrahigh-vacuum conditions (10^{-10} Torr). Surface structure and purity were monitored by LEED and Auger electron spectroscopy. Tests confirmed that the ELS data was not affected by surface impurities at the levels present in the final stages of surface preparation.

A typical experimental electron energy-loss spectrum is shown in Fig. 1 for two values of the primary electron energy E_p. The $3p$ excitation appears as a dip-peak feature with increasing energy loss. This is the "steplike" line shape noted in earlier ELS work, and has been termed the "soft-x-ray edge" when viewed optically. The structure of the optical absorption spectrum in the vicinity of this edge has been associated[1,3,9] with transitions from the $3p$ core level to the empty states of the $3d$ conduction band, taking into account the lifetime broadening of the $3p$ hole. However, the dispersionlike shape of our ELS spectrum (see Fig. 1) and the fact that the calculations were not able to reproduce the dip that occurs in optical absorption on the low-energy side (see Figs. 3 to 6, Ref. 9) led us to assume that a resonant interaction between a discrete final state and a continuum of final states was present and was responsible for the line shape.

To confirm this point we have performed a simplified atomic calculation in which we assume that the excitation process can be approximately calculated with wave functions of one Ni ion (we neglect matrix elements connecting different Ni atoms). The initial state is Ni^+ in the configuration $3p^6 3d^9; {}^2D$ and the discrete final state is $|\varphi\rangle \equiv 3p^5 3d^{10}; {}^2P$. We neglect the spin-orbit splitting of the $3p$ hole here, but consider it below. The continuum states that mix with $|\varphi\rangle$ are $|\Psi_{\epsilon f}\rangle \equiv 3p^6 3d^8 \epsilon f; {}^2P$ and $|\Psi_{\epsilon p}\rangle \equiv 3p^6 3d^8 \epsilon p; {}^2P$, where ϵ is the excitation energy. The mixing is due to the Coulomb interaction and the corresponding matrix elements are proportional to the Slater integrals $R_K(3d, 3d; 3p, \epsilon f)$ and $R_K(3d, 3d; 3p, \epsilon p)$. These matrix elements are precisely those which are responsible for the Coster-Kroning processes which determine the lifetime of the $3p$ hole,[9] and they have been tabulated by McGuire.[10] The values of $R_K(3d, 3d; 3p, \epsilon p)$ are considerably smaller than those of $R_K(3d, 3d; 3p, \epsilon f)$ so that we neglected the continuum having an outgoing p wave. The only multiplets of d^8 that can combine with ϵf to give ${}^2P$ are ${}^1G$, ${}^3F$, and ${}^1D$, so that we have the case of one discrete level $|\varphi\rangle$ interacting with three continua.

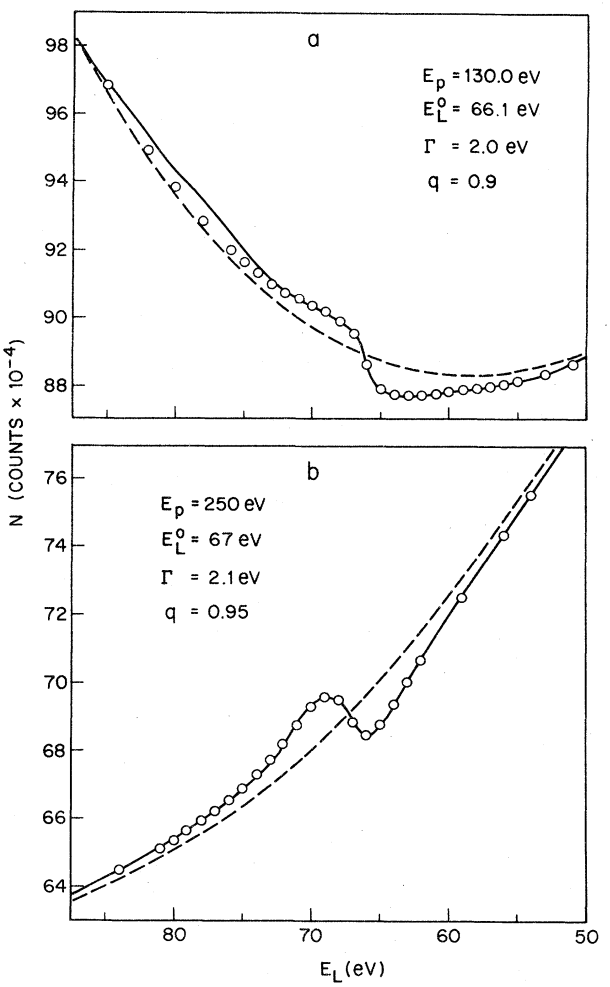

FIG. 1. Plots of the electron energy-loss distribution for Ni(001) in the vicinity of the $3p$ excitation for two different values of the primary energy E_p. The full lines are experimental $N(E_L)$ curves. The circles indicate values calculated from Eq. (1). The background curves $N_0(E)$ (broken lines) and the values assigned to M^2 in Eq. (1) were (a) $N_0(E) = 285.21 - 46.593E^{1/2} + 2.7566E$, $M^2 = 0.9$; (b) $N_0(E) = 954.50 - 142.42E^{1/2} + 5.691E$, $M^2 = 1.3$. The background parameters were generated by assuming that the contribution of the resonance to the background was negligible at points 25 eV on either side of E_L^0. The value of the background at E_L^0 was then taken as a parameter and adjusted along with Γ and q so as to give a best fit. Using this procedure a unique fit could be obtained for the parameters to within the uncertainties quoted in the text.

The line shape as given by Fano[6] for such a

case is

$$N(E_L) - N_0(E_L) = M^2[q^2 - 1 + 2q\epsilon(E_L)]/[1 + \epsilon(E_L)^2], \quad (1)$$

where $N_0(E)$ is a smooth "background" function representing the sum of coherent and incoherent continua, q is a line-shape parameter which is obtained by diagonalizing the interaction matrix of $|\varphi\rangle$ with the three continua, and $\epsilon = (E_L - E_L^0)/\Gamma$ where E_L is the energy loss, E_L^0 is the position of the discrete level, and Γ is half the linewidth.

The use of atomic loss-spectroscopy states for describing the Ni atoms in the metal may appear as a drastic assumption. However, it is not difficult to show that as long as matrix elements of the dipole operator and of the Coulomb interaction between neighboring Ni atoms are neglected, the value of q obtained in this fashion is the same as the value obtained when the d electrons are treated in the tight-binding approximation. The reason for the identity of the two results is that both the $3d$ bandwidth and the atomic multiplet splittings are small compared to the $3p \rightarrow 3d$ excitation energy so that the value of the dipole matrix element for the $3d \rightarrow \epsilon f$ is essentially constant in that energy range.

A fit to the experimental line shape using Eq. (1) may be obtained by representing $N_0(E_L)$ with a smooth curve that approaches the experimental $N(E_L)$ curves far from the $3p$ excitation. The fit to the $3p$ line shape is illustrated in Fig. 1 for two values of E_p. In both cases the fit in the vicinity of the transition is good for nearly identical values of the Fano parameters in spite of the very different shape of the background (broken lines in Fig. 1) in the two cases.

The best values of the $3p$ line parameters from the above fit are $E_L^0 = 66.1 \pm 0.2$ eV, $\Gamma = 2.0 \pm 0.2$ eV, $q = 0.9 \pm 0.1$. These values were obtained for each of several experimental curves obtained for different values of the primary energy E_p between 100 and 200 eV [e.g., Fig. 1(a)]. Slightly higher values were obtained for higher values of E_p [e.g., Fig. 1(b)] because of diminished energy resolution.

The above value of E_L^0 is in good agreement with the value obtained from the optical spectrum[1,3] by taking the midpoint between the maximum and minimum, namely 66.1 eV. The Fano-type line shape is not clearly present in the optical results for Ni, but it is in the cases of Mn, Fe, and Co. However, the asymmetry of the optical line shape is consistent with the electron-scattering data, and with the theory discussed below.

To compare experiment with theory, the empirical parameters Γ and q may be related to the relevant matrix elements according to $\Gamma = \pi V^2$ and $q = P/\pi MV$, where $P = (3p|r|3d)$, $M = (3d|r|\epsilon f)$, and $V = (d, d|v_C|p, f)$, the latter being the matrix element of the Coulomb interaction. The radial parts of these matrix elements were kindly furnished by Dr. McGuire. In summary, the following values were used:

$$R_1(dd; pf) = 14.1 \times 10^{-2} \text{ a.u.}, \quad R_3(dd; pf) = 7.78 \times 10^{-2} \text{ a.u.},$$

$$(3p|r|3d) = 0.786 \text{ a.u.}, \quad (3d|r|\epsilon f) = 0.396 \text{ a.u.},$$

where each orbital is taken with the same phase factor in all the matrix elements and the continuum orbitals are normalized per rydberg. The result of the calculation is $q = 1.8$ and $\Gamma = 2.0$ eV. Considering the roughness of the calculation and our neglect of the backscattering of the outgoing wave by the other Ni atoms, which will affect the value of the transition matrix element and hence of q, the agreement with the experimental value is satisfactory.

Our use of the dipole approximation for the transition matrix elements $3p \rightarrow 3d$ and $3d \rightarrow \epsilon f$ requires an explanation. The geometry of the experiment is such that only electrons which have suffered a deflection θ greater than 100° are counted. At $\theta = 100°$, the momentum transfer κ is 4 and 5.6 a.u. for incident electron energies of 130 and 250 eV, respectively, and the dipole approximation has completely broken down. The destructive interference between contributions of different r values in the expression of the matrix element greatly reudces the values of the transition matrix elements compared to their dipole-approximation values. If the inelastic scattering occurs in the forward direction the corresponding values of κ are 0.9 and 0.6 a.u., respectively. Inspection of the wave functions shows that the dipole approximation is nearly valid for these κ values. Consistent with the forward-peaked character of the inelastic differential cross section we assume that the dominant electrons which contribute to our signal are those that have been inelastically forward scattered and have in addition suffered elastic backward scattering. This assumption is also consistent with the fact that the q values measured at incident energies of 130 and 250 eV are nearly identical while the corre-

sponding κ values are widely different.

We now consider the effect of the spin-orbit splitting of the $3p$ hole, which is expected to be about 2 eV.[3] There are now two discrete levels, $p_{3/2}$ and $p_{1/2}$, interacting with the continua, and the line shape becomes more complex. In the general case where a given continuum state interacts with *both* discrete levels the transition amplitude vanishes at two energy values,[6] which, if it were the case here, would seriously alter the expected line shape. However, in the present case the outgoing continuum states must also be labeled with j values and in the atomic approximation a given continuum state interacts only with the discrete state having the same j value. The resulting line shape is the superposition of two lines with identical q and Γ values, separated by the $3p$ spin-orbit splitting and with an intensity ratio of 2:1 for the $\frac{3}{2}$:$\frac{1}{2}$ states. Tests showed that such a superposition gives as good a fit to the observed line shape as does a single level, provided, however, that the assumed value of spin-orbit splitting does not exceed 1.6 eV; for larger assumed values the shape of the loss spectrum is distorted to an extent that would be perceptible in the present experiments. With an assumed spin-orbit splitting of 1.6 eV the best value of Γ from the fit is 1.5 eV.

Finally, we believe that the line shape observed in these experiments is not related to the s-d mixing which has been the subject of recent papers.[11] Our reasons for this are twofold: First, the resonance width 2Γ of a single Ni ion in Cu metal is of the order 0.6 eV,[12] which is considerably smaller than the observed value of 4 eV, and second, the parameter q for s-d mixing can be shown to be negative while the fact that the dip in the absorption is on the low-energy side requires a positive value of q.

The more symmetrical shapes seen in the optical and ELS spectra of Ti, V, and Cr are expected since q will increase as the number of d electrons decreases. However, we do not understand the splittings observed in the optical spectra of these metals nor can we account for the apparent lack of multiplet structure in Mn, Fe, and Co. For reasons given above, no such structure is expected in Ni.

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