Comparison between extended x-ray-absorption and extended electron energy-loss fine-structure results above the $M_{2,3}$ edge of cobalt

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An electron energy-loss fine-structure (EELFS) experiment has been carried out above the $M_{2,3}$ edge of a cobalt single crystal. These results are compared with extended x-ray-absorption fine-structure (EXAFS) data taken on the same sample (and using the same experimental apparatus) by using the partial-yield technique. The use of the usual EXAFS analysis on the two sets of data gives practically identical results (within experimental accuracy). However, the nearest-neighbor distance that can be calculated by using theoretical phase shifts [W. Ekardt and D. B. Tran Thoai, Solid State Commun. **45**, 1083 (1983)] is less in both cases by about 0.2 Å with respect to the known value. We conclude that the matrix element involved in the energy-loss excitation of the Co $M_{2,3}$ core level in the EELFS experiment has a prevalent dipole contribution. This important result implies that the usual EXAFS analytical technique for determining lattice parameters can also be applied to EELFS data. We conclude also that the theoretical phase shift calculated within the $Z+1$ approximation is not adequate for the analysis of $3p$-edge fine structures.

INTRODUCTION

The surface extended x-ray-absorption fine-structure (SEXAFS) technique has been shown to be one of the most powerful for determining the local geometry of adatoms on surfaces.[1,2] The greatest attraction of this technique resides in the simplicity of the analytical procedure for extracting the structural information from the experimental data.[3] Unfortunately, the number of synchrotron radiation facilities where meaningful SEXAFS data can be obtained is very small.[4] This is probably the reason why the number of structural determinations with this technique is still rather limited.

Recently a new similar technique was proposed,[5,6] which is based on the detection of the fine structure present in a reflection energy-loss experiment, above the structure originating from core-level excitations. This technique called surface extended energy-loss fine structure (SEELFS), is extremely attractive for its experimental simplicity and puts accurate structural determinations within the reach of every surface-science laboratory. Successful nearest-neighbor and next-nearest-neighbor distance determinations have been obtained for carbon[7] and oxygen[8] on Ni and for other systems.[9] The first application of this technique was reported for an analysis of the fine structures above the $M_{2,3}$ core levels of Cu and Ni.[6] Strictly speaking, this experiment should have been termed EELFS since the depth probed is about 10—20 Å. While this work demonstrated for the first time the geometrical content of these structures, the lattice parameters determined using the available phase shifts were 0.2 Å too short with respect to the known crystallographic data. Criticism arose about the possibility of using the EXAFS formalism for a process that involves a Coulomb matrix element (which reduces to usual dipole matrix element only in the limit of small momentum transfer[10–13]). However, in view of the success of many structural determinations using K (Refs. 7 and 8) and $L_{2,3}$ edges (Ref. 14), we felt a deeper experimental investigation of the energy-loss process involving a $3p$ edge ($M_{2,3}$) was worthwhile.

In the following we report on the comparison of EELFS and EXAFS data, taken on the same sample [Co(001)] and with the same experimental apparatus. The most interesting version of the new technique using electrons is its surface counterpart (SEELFS). However, we

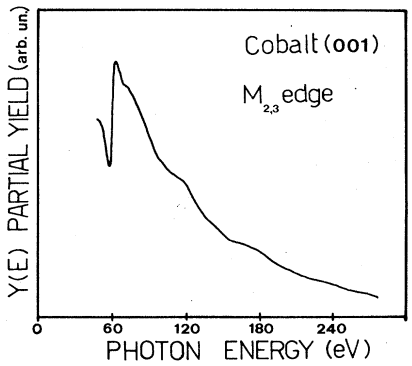

FIG. 1. Partial-yield spectrum ($E_{kin}=0-3$ eV) of Co(001) above the $M_{2,3}$ edge.

are now interested in improving the understanding of the basic physics phenomena in which the technique works. We have therefore chosen to compare "bulk" results for minimizing experimental problems and uncertainties. Within the experimental limits, the optical data give the same nearest-neighbor distance as the electron-loss experiment. This finding confirms, beyond reasonable doubt, the applicability of the usual simple EXAFS formalism for the analysis of EELFS results. It is interesting to note, however, that *both* EXAFS and EELFS data analyzed by using the phase shifts available in the literature[15] give a shorter lattice parameter (by about 0.2 Å). Our results therefore point out the inadequacy of calculating $M_{2,3}$ phase shifts by using the unscreened $Z+1$ ion approximation[15] for the first-row transition metals.

EXPERIMENT AND RESULTS

The EXAFS data were taken using the Grasshopper beam line of the Frascati Synchrotron Radiation Facility. The absorption coefficient of a Co(001) surface was measured by using the partial-yield technique (monitoring a 3-eV energy window centered on the secondary-electron distribution). This experimental configuration was chosen to obtain information pertaining to the bulk of the sample (the estimated sampling depth is several tens of Å), avoiding surface-related complications.[16] The light impinged at 45° on the sample surface, and the electrons were detected by using a cylindrical mirror analyzer with its axis tilted 45° with respect to the normal to the sample. The experimental spectra were corrected for the second-and third-order light contributions and normalized with respect to the photon flux by measuring the yield of a graphite sample.

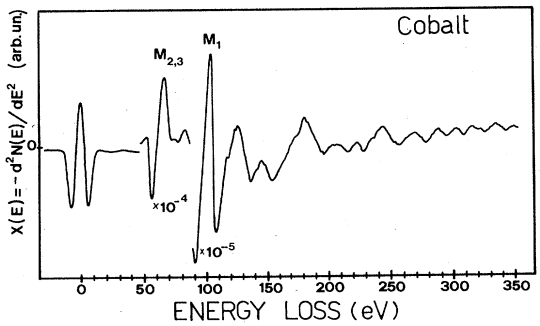

FIG. 2. Extended energy-loss fine structures (EELFS) detected above the $M_{2,3}$ cobalt core level. The primary-beam energy was 2000 eV and the peak-to-peak voltage modulation $V_{p.p.}$ was 8 V.

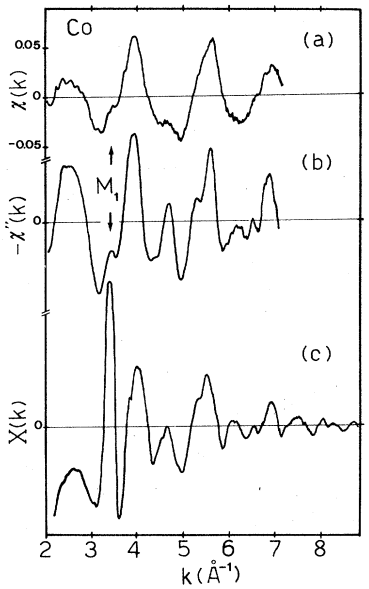

FIG. 3. Comparison between the EXAFS $\chi(k)$ signal extracted from the data of Fig. 1 [panel (a)], with the EELFS signal of Fig. 2 [panel (c)]. The second derivative $-\chi''(k)$ of the EXAFS $\chi(k)$ signal is reported in panel (b). The spectra are displayed as a function of the wave vector k (Å^{-1})$=[(2m/\hbar^2)(E-E_0)]^{1/2}$, and the edge E_0 was chosen at the inflection point of the $M_{2,3}$ threshold. Note that the M_1 edge gives a contribution much larger in EELFS than in EXAFS, pointing to a nonvanishing momentum transfer.

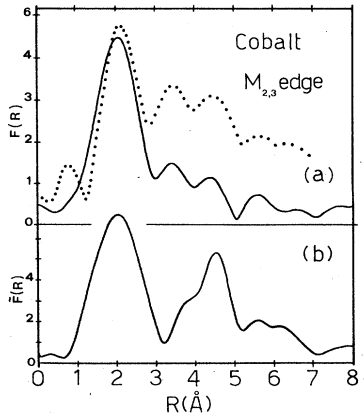

FIG. 4. (a) $F(R)$ radial distribution as obtained from the Fourier transform of the $\chi(k)$ EXAFS signals of Fig. 3(a) (solid line). The dotted line represents the Fourier transform of the second derivative $-\chi''(k)$ of the EXAFS signal. (b) $F(R)$ obtained from the EELFS data of Fig. 3(c). The Fourier transforms were performed using the same k integration range for the three experimental spectra.

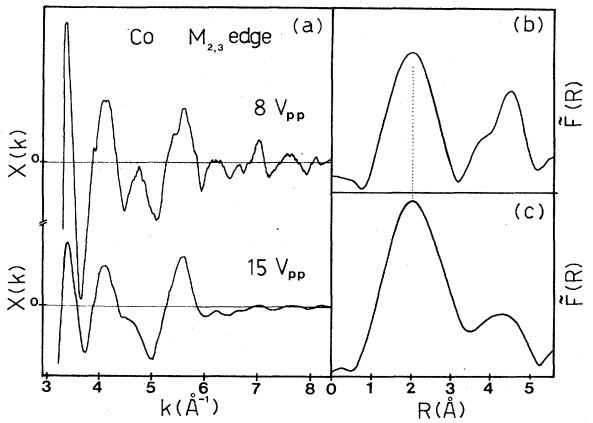

FIG. 5. (a) Effect of experimental resolution on the EELFS data. The spectra were detected using a modulation voltage $V_{\text{p.p.}}$ of 8 V (upper curve) and 12 V (lower curve). Their Fourier transforms (between 3.5 and 8.5 Å^{-1}, for both spectra) are reported in panels (b) and (c), respectively.

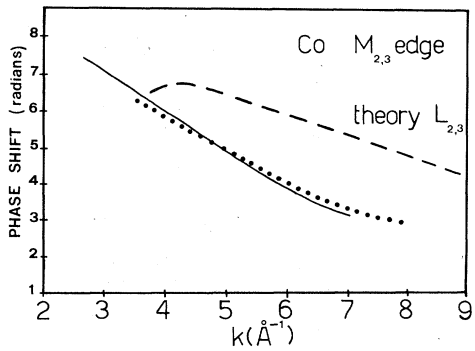

FIG. 6. Comparison between the experimental cobalt $M_{2,3}$ phase shift extracted from the EXAFS (solid line) and EELFS (dotted line) experimental data. The Teo and Lee theoretical phase shift (Ref. 15), computed for the Co-$L_{2,3}$ edge, is also reported (dashed line).

Figure 1 shows the partial-yield spectrum $Y(E)$ of the cobalt single crystal in the (50—280)-eV photon-energy range. The edge at $\sim$60 eV is due to the $3p$-electron excitation and shows the characteristic Fano-resonance line shape.[17] EXAFS structures appear as small bumps at about 120, 145, 180, and 240 eV. The overall agreement with absorption data by Sonntag, Haensel, and Kunz[18] is good (these authors, however, failed to detect the weak EXAFS structures). Figure 2 shows the second derivative of the electron-energy distribution $X(E)$ of the same Co sample, taken with a primary-electron energy $E_p=2000$ eV and extending more than 300 eV above the $M_{2,3}$ edge.

ANALYSIS OF THE DATA

The oscillatory contribution $\chi(k)$ of the absorption spectrum is shown in Fig. 3(a). The **k**-space transformed loss spectrum $X(k)$ is shown in Fig. 3(c). Since we want to obtain a detailed comparison of the results of the two different techniques we need to treat the data in the same fashion. Accordingly, the second derivative $-\chi''(k)$ of the function $\chi(k)$ has been calculated and used in the analysis. The function $-\chi''(k)$ is shown in Fig. 3(b). By comparing Figs 3(b) and 3(c) it is apparent that the spectra are quite similar (with the exception of the M_1 contribution). The principal structures, however, coincide to within 0.05 Å^{-1}.

The Fourier transforms of these functions are shown in Fig. 4. The main peak in all these radial distribution functions falls at 2.05 Å (to within 0.05 Å). This very important result shows, beyond any reasonable doubt, that the energy-loss data can be reliably analyzed with the same EXAFS formalism used for reducing optical data. Figure 5 shows a comparison between SEELFS data taken with different resolutions. The data obtained with poorer resolution (peak-to-peak voltage modulation $V_{\text{p.p.}}=15$ V) produce a peak in the Fourier transform which is considerably broader than that obtained with improved resolution ($V_{\text{p.p.}}=8$ V). It is important to note, however, that the position of the first peak stays constant. Since the original experimental data were taken over a limited energy range, the position of the next-nearest-neighbor shells is not very reliable and will not be considered.

As is well known, the radial-distribution data obtained from the EXAFS analysis should be corrected by an appropriate phase-shift contribution. The corrected $F(R)$ is given by[19]

$$F(R)=\int_{K_1}^{K_2}\chi(k)\exp[-2ikR+\Phi_{\text{theor}}(k)]dk\ . \qquad (1)$$

In this way the correct crystallographic lattice parameters may usually be obtained in an EXAFS experiment to within an accuracy of ± 0.01 Å.[3(b)] We have evaluated $F(R)$ as given by Eq. (1) using our experimentally determined $\chi(k)$ and the $\Phi_{\text{theor}}(k)$ computed for the $L_{2,3}$ edge of Co by Teo and Lee.[15] Ekardt and Tran Thoai[20] have shown recently that with the $Z+1$ approximation the phase shifts of the $L_{2,3}$ and $M_{2,3}$ edges of Cu and Ni give identical results. With this correction, the first peak in $F(R)$, for both the SEELFS and optical data, shifts to 2.31 Å. hcp cobalt has two nearest-neighbor subshells of six atoms located at 2.49 and 2.51 Å, respectively.[21] This mismatch of $\sim$0.2 Å shows that the theoretical phase shift we have used is not adequate.

An experimental determination of the phase shift can be obtained from the known lattice parameter by back-Fourier-filtering[3] of the first peak of $F(R)$. Figure 6 illustrates the results for the optical (solid line) and EELFS (dotted line) experimental phase shifts. The agreement between the two once again gives good support to the concept that the scattering matrix element of the loss experiment is nearly identical to the optical dipole matrix element.[6,14] In Fig. 5 the theoretical $L_{2,3}$ phase shift of Teo and Lee[15] is also reported. We also conclude at this point that the mismatch previously found by analyzing EELFS data above the $M_{2,3}$ edges of Ti, Fe, Ni, and Cu is not intrinsic to the applicability of the technique, but rather results from the inadequacy of the theoretical phase shifts for the $3p$ core levels. One possible reason for this inade-

quacy could be the rather extended nature of these shallow core levels (~ 0.2—0.3 Å). Another possibility is related to the autoionizing effects, which are particularly strong at the edge (Fano effects).[17]

ACKNOWLEDGMENT

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