Single x-ray photon excitaton of two and three electrons in nickel

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Cooperative single-photon excitations of two $(K+L)$ and three $(K+L+M)$ electrons in nickel were studied using x-ray absorption spectroscopy. Each of the edges detected has an energy higher by about 164 ± 3 eV than the sum of those required for exciting the electrons involved independently. The probabilities for the two- and three-electron excitation are found to be 0.25% and 0.08%, respectively, of that for a single K-electron excitation.

Although predicted as early as 1925,[1] multielectron one-photon transitions in metals received serious experimental attention only recently, following the heavy-ion–atom collision of Wolfli et al.[2] The considerable probability of creating multiple vacancies in such collisions enabled fluorescence spectroscopy measurements to be carried out with reasonable accuracy. Energy-level determinations of multiply ionized atoms based on these experiments were, however, encumbered by insufficient knowledge of the number and distribution of the vacancies produced in the higher levels of the atoms investigated.[3]

Two-electron–one-photon edges were detected first and, until recently, only in x-ray absorption spectra of inert gases.[4,5] The relatively high probability of double-vacancy creation, only one order of magnitude below that of the single K^{-1} creation, and the relative absence of K-edge fine structure in these monoatomic gases, allow absorption studies to be carried out with relative ease, as exemplified by the very detailed work of Deslattes et al.[5] on Ar, published while the present study was in progress. Threshold studies of multivacancy satellites in the emission and Auger spectra of various solids and gases[6] as well as several related absorption studies in the optical region[7] and energy-dependent photoionization studies of inert gases[8] and Be (Ref. 9) were also published.

For solid elements, however, multiple-vacancy x-ray absorption spectroscopy is hampered by the prohibitively low probabilities of multivacancy creation, which are three orders of magnitude lower than that of the K^{-1} creation. A further complication is the extended x-ray absorption fine structure (EXAFS) associated with the K edge which completely masks the KM multivacancy spectra and allows only those KL spectra measurements where the edges lie at least 700 eV above the K edge. For these reasons the first multiple-vacancy x-ray absorption spectra for solids were published only very recently by Salem and co-workers.[9-13] In these measurements, however, the size of the double-vacancy edge is between 0.3% and 0.5% of the intensity, while the mean standard deviation due to counting statistics is between 1.5% and 0.7%. Under these conditions definite detection and identification of edges is extremely difficult and the energy levels and, in particular, the cross sections deduced are of rather low accuracy. To our knowledge no observations of multiple-electron–one-photon excitations in x-ray absorption spectra of solid elements have been published previously.

We report here x-ray absorption measurements of two-electron–one-photon and three-electron–one-photon excita-

tions in Ni with edge discontinuities of 0.30% and 0.18% in intensity, respectively, with counting statistics having a mean standard deviation of 0.15%, thus making the detection and identification of the edges definite. The experiment was carried out at the Daresbury Laboratory Synchrotron Radiation Source run at 2 GeV and 100 mA. The sample was a 5-μm-thick Ni foil of 99.99+ purity. Relevant impurity content was such as to preclude any possible contamination of the spectrum in the range of energies explored. A perfect silicon crystal monochromator employing two symmetric 511 reflections in a groove was used for energy scanning. The 2 sec of arc vertical divergence of the synchrotron beam[14] provided an energy resolution of $dE/E = 10^{-5}$. Post-sample monochromatization was employed to prevent beam "walk" across the sample and the resulting intensity changes caused by possible sample thickness variations. A high-purity germanium detector was used in conjunction with a single-channel pulse-height analyzer to eliminate the small amount of harmonics passed by the monochromator. Intensity was kept within the limits of linear response of the detector. Data collection was carried out under microcomputer control.[15]

Signal averaging,[16] i.e., summation of a large number of short repeated scans rather than a single long run was employed to eliminate structure originating in sudden small intensity changes, known to occur in synchrotron sources.

The energy range of interest was scanned first with the Ni sample in the beam path then with two foils, one of Cu and one of Zn, in the beam path. The sharp K edges of these metals provided excellent energy scale calibrations for the scan. Finally, a scan without any sample was done. This was necessary to ensure that no intensity changes occurred by many beam simultaneous reflections in the monochromator, nonuniform detection efficiency across the detector, etc. The spectra measured in the three scans is given in Fig. 1. To improve detectability of the very small intensity changes found, only differences between the data points and a straight line connecting the first and last data points are plotted in Figs. 1(a) and 1(b). No other treatment was applied to the data and, in particular, no smoothing was employed so that the scatter of the points reflects the true statistics of the measurements. The total number of counts collected for each point was over 4.5×10^5. The absorption edges of the various multielectron excitations are clearly visible in Fig. 1(a), as well as in spectra obtained in four additional runs done with the beam hitting different spots on the sample, thus establishing beyond doubt, the existence of these features in the absorption spectrum of Ni. Note the
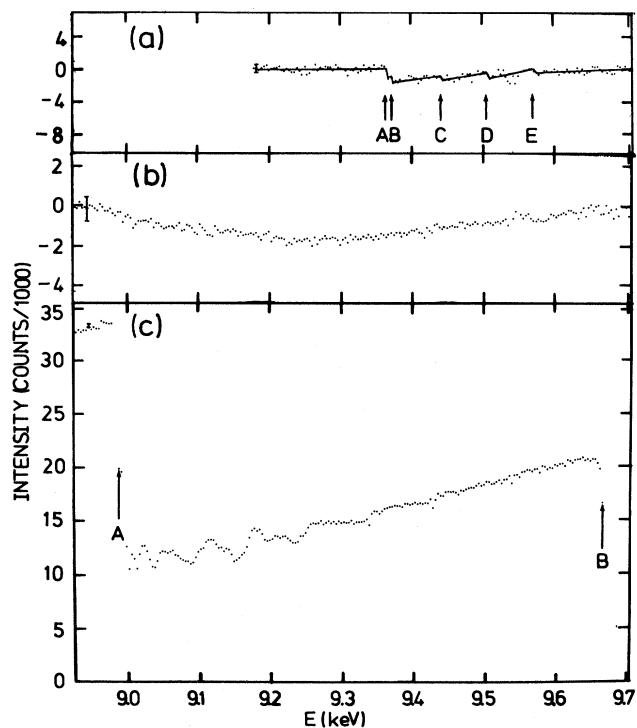
FIG. 1. Energy spectra: (a) two- and three-electron–one-photon excitation spectrum. The edges marked are $A - 1s^{-1} + 2p_{3/2}^{-1}$, $B - 1s^{-1} + 2p_{1/2}^{-1}$, $C - 1s^{-1} + 2p_{1/2,3/2}^{-1} + 3p_{1/2,3/2}^{-1}$, $D - 1s^{-1} + 2s^{-1}$, $E - 1s^{-1} + 2s^{-1} + 3p_{1/2,3/2}^{-1}$. (b) Spectrum obtained without sample. Note the smooth, structureless curve with only one significant spurious intensity change at 9.530 keV. The corresponding intensity change is noticeable in (a) at the same energy. (c) K-edge spectrum of a sample made of a foil of Cu (A) and of Zn (B). The sharp edges provide excellent energy calibration. (a) and (b) are difference plots, and the error bars indicate ± 1 mean standard deviation of the data. For details see text.

relatively large intensity changes at 9.530 keV. These are probably due to simultaneous reflections in the monochromator as the large corresponding intensity changes at the same energy in Fig. 1(b) indicate. The indispensability of the no-sample scan for eliminating spurious structure in the spectrum is thus demonstrated. The edges seen in the fig-

ure are over 1000 eV from the Ni K edge. Thus they are well beyond the ~ 700-eV range of detectable EXAFS associated with the K edge.[17] Furthermore, their shape is completely different from the smooth undulations of the absorption fine structure. Thus the possibility of attributing these edges to EXAFS is excluded. The clear signature of the closely spaced $1s^{-1} + 2p_{1/2}^{-1}$ and $1s^{-1} + 2p_{3/2}^{-1}$ edges provides a good starting point for edge identification. The assignment and energies of the various edges are summarized in Table I. Theoretical values were calculated using the $z + 1$ approximation[18] with experimental single excitation energy levels.[19]

The 9.437-keV edge presents a particular problem. Is it the doublet $1s^{-1} + 2p_{1/2}^{-1} + 3p_{1/2,3/2}^{-1}$, the doublet $1s^{-1} + 2p_{3/2}^{-1} + 3p_{1/2,3/2}^{-1}$, or an unresolved sum of both? A close examination of the data reveals that this edge is marginally higher than the two-electron–one-photon edge and is roughly twice the height of the other three-electron–one-photon edge at 9.568 keV. This and the somewhat broader width of the edge seem to favor the last possibility, namely, an unresolved quadruplet $1s^{-1} + 2p_{1/2,3/2}^{-1} + 3p_{1/2,3/2}^{-1}$.

The shifts obtained in this experiment are larger by about 55 eV than those reported by Salem et al.[11] for Zn. Whether this is a result of the different type of sample used (metal foil in our case versus powder in Ref. 11) is unclear. Deviations of the same order of magnitude, although smaller by a factor of 2 were, however, found for Sm $2s^{-1} + 2p^{-1}$ (25 eV)[13] and Se $1s^{-1} + 2s^{-1}$ (26 eV)[12] between the measured values and relativistic Hartree-Fock-Slater calculations. The transition energies obtained from the $z + 1$ approximation are considerably lower than our measured values, unlike the inert gases results where they agree to within the experimental error. Note, however, that although the difference is not as large as here, the $z + 1$ approximation yields consistently too low multivacancy energies for Zn (Ref. 11) and Se (Ref. 12) as well, the largest deviations, 14 and 17 eV for Se and Zn, respectively, being in the $1s^{-1} + 2p_{3/2}^{-1}$ level, where the $z + 1$ approximation is expected to work best.[18] Our double-vacancy shifts follow the expected[9-12] pattern: roughly equal shifts for the double vacancies involving the $2p$ electrons and a smaller one, by about 10 eV, for the excitation involving the $2s$ electron. The same pattern is revealed for the three-electron transitions as well. The differ-

TABLE I. Energies of the two- and three-electron simultaneous excitation edges measured. Shifts of these edges relative to the sum of the energies required for exciting the electrons involved independently are also listed. The number in parentheses is the uncertainty in the last digit of the energy. Theoretical values were calculated using the $z + 1$ approximation and energy levels from Ref. 19.

Transition	Energy (keV)	Theory (keV)	Energy shift (eV)
$1s^{-1}$	8.3328(4)[a]		
$2s^{-1}$	1.0081(4)[a]		
$2p_{1/2}^{-1}$	0.8719(4)[a]		
$2p_{3/2}^{-1}$	0.8547(4)[a]		
$3s^{-1}$	0.1118(6)[a]		
$3p_{1/2,3/2}^{-1}$	0.0681(4)[a]		
$1s^{-1} + 2s^{-1}$	9.501(3)	9.429	160
$1s^{-1} + 2p_{1/2}^{-1}$	9.372(3)	9.284	167
$1s^{-1} + 2p_{3/2}^{-1}$	9.358(3)	9.264	170
$1s^{-1} + 2s^{-1} + 3p_{1/2,3/2}^{-1}$	9.568(5)	9.503	159
$1s^{-1} + 2p_{1/2,3/2}^{-1} + 3p_{1/2,3/2}^{-1}$	9.437(6)	9.357	164
		9.338	

[a] Reference 19.

ences in energy between the various edges in Table I follow rather closely the differences in energy between the single-electron excitations involved, as revealed by the almost equal shifts listed. Note that the three-electron–one-photon excitations involving the $3s$ electron were not detected in this study. This may be due to the relatively small number of the $3s$ electrons which would result in a cross section well below the statistical accuracy of our data.

By comparing the sizes of the various edges in Fig. 1(a) to that of the Ni K edge it is possible to derive the ratios of the corresponding cross sections.[9-13] The accuracy of the values thus obtained is, however, rather low due to the small step height of the multielectron edges. Our data indicate that all the double excitations detected have roughly equal cross sections, which seems to point to the shake-up type[20] of absorption process. The ratio of the two-electron–one-photon cross section $\sigma(2)$ to that of the single $1s^{-1}$ excitation $\sigma(1)$ is

$$\sigma(2)/\sigma(1) = (2.5 \pm 0.4) \times 10^{-3} \ . \tag{1}$$

This value agrees well with those reported[9,11,12] for Ge, Zn, and Se, but is smaller by an order of magnitude than the value of 2×10^{-2} deduced[9] for Ne and Ar (Ref. 4) and the value of 3.5×10^{-2} which can be deduced from Figs. 4 and 5 in Ref. 5. As for the three-electron–one-photon edges, if we assume, as discussed above, that the 9.437-keV edge is

an unresolved quadruplet and the one at 9.568 keV is a doublet, then all the three-electron–one-photon cross sections are, again, roughly equal and

$$\sigma(3)/\sigma(1) \simeq (0.8 \pm 0.3) \times 10^{-3} \ .$$

This value should, however, be regarded as highly tentative until much more accurate data become available.

The measurements presented here demonstrate for the first time unequivocally the existence of a complete spectrum of two- and three-electron–one-photon excitations for a metal. While our data allow for an accurate determination of the energy levels involved and, to a lesser extent, the cross sections for the various excitations, additional measurements on as large a number of elements as possible will be required for gaining a detailed understanding of the processes involved in multielectron–one-photon excitations of atoms by x rays. This is particularly desirable in view of the apparently contradicting results obtained for inert gases and metals. Further work on this problem is currently in progress.

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