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Core hole effects on electronic structure: Al in AlNi

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Abstract. We have studied experimentally and theoretically the effect of the core hole on the local density of both occupied and unoccupied states at a core ionised Al site in AlNi. We compare calculated local Al p and s state densities with experimental data for x-ray emission (XES), Auger (AES) and x-ray absorption (XAS) spectroscopy, which reflect the local DOS in the absence (KV and LV XES) and in the presence (KLV Auger and XAS) of a core hole. From this comparison we conclude that core hole effects are appreciable, although their precise determination is hindered by self-energy effects in this particular system. These results suggest that interpretation of the K-edge x-ray absorption spectra of light elements like Al in alloys and compounds in terms of one-particle groundstate DOS is in general inappropriate.

In many forms of high-energy spectroscopy a core hole is either created or destroyed. Thus understanding of the nature of the modification of the electronic structure of a solid by a core hole is important and a prerequisite of the use of any high-energy spectroscopic technique for studying the detailed electronic structure of materials. This is particularly true for x-ray absorption spectroscopy (XAS), which is one of the easiest and most versatile experimental techniques, but which causes a core hole to be left in the final state after the transition. Our aim in this paper is to study the effect of the core hole on the local density of both occupied and unoccupied states at a core ionised Al site in AlNi and to relate this to effects found in other systems.

For XAS the ground state is well defined, but a core hole is present in the final state and the spectral distribution in such cases usually reflects the electronic structure of the final state with the core hole [1–4]. In addition, the radial integrals determining the intensity of the transition are short-ranged, so that the spectral shape reflects the local (and symmetry selected) density of states (DOS) at the core ionised site. The relative influence of solid-state, band-structure effects depends on the relative size of the monopole and multiplet interactions between the core hole and valence electrons V_{cv} and the valence bandwidth W [5]. When V_{cv} is large and W is small (e.g., for the 4f states) then the core hole potential effects dominate (see e.g. [6–8] and references therein). It is also known that if V_{cv} and W are comparable, then the core hole and band structure effects

are both important for the spectral shape. The transition metal $L_{2,3}$ edges, where V_{cv} is from 2–8 eV and W is from 4–10 eV, are such intermediate cases in XAS ([9] and references therein, [10, 11]). There are, however, no general guidelines for the influence of the core hole on XAS spectra in the very large group of spectra when V_{cv} is smaller than W , and this is a case we address here†.

Although solid-state band structures, and even the local DOS at a core-ionised site can now be computed with great reliability, this is not enough. For comparison with spectroscopic measurements it is necessary to go beyond the local-density approximation and to include further corrections to the electron–electron interaction through appropriate treatment of the electron self-energies ([12], [13] and references therein, [14–17]), and this still poses severe problems‡. We thus fall back on a comparison of independent experiments, as well as comparison between experiment and the predictions of a one-particle theory, to isolate the effects which interest us§.

For a few light metals KLV Auger spectra offer an almost unique probe of the occupied DOS at a core-ionised site, because a core hole is present both in the initial and in the final states of the system. Comparison with x-ray emission spectra (XES) then allows us to isolate the influence of the core-hole potential [19–23]. Comparison of x-ray emission spectroscopy (XES), Auger emission spectroscopy (AES) and photoelectron spectra with computed DOS then allow us to estimate the appropriate self-energy corrections. Finally we note that XAS and XES are not only local probes but, being subject to the dipole selection rules ($\Delta l = \pm 1$), are also symmetry selective; similarly the angular parts of the Auger matrix elements lead to different weighting of states of different angular momentum, as discussed below. This symmetry selectivity is important for a full characterisation of the core-hole effects.

The samples used for this investigation were prepared by melting together the requisite quantities of pure Al and Ni under pure argon. Metallographic methods and x-ray powder diffraction were used to check that the level of impurity phases was less than 5% and thus too low to influence the spectroscopic results significantly. The samples were cleaned by scraping under vacuum immediately prior to measurements. X-ray emission spectra were excited by electron bombardment. The x-ray absorption data were accumulated in total-electron-yield mode. The Auger spectra were excited using bremsstrahlung radiation from a Ti anode, with a Be window separating the sample from the anode chamber to avoid contamination of the sample.

The methods for computation of the DOS are described elsewhere [24]. Briefly, we used the Korringa–Kohn–Rostoker Green function method, which is particularly suited for these studies. The perturbation arising from the core hole on the Al site is treated by calculation of the local DOS of a Si impurity in AlNi ($Z + 1$ approximation). The self-consistent calculation includes the impurity site and its eight first-nearest-neighbours.

For comparison with experiment the DOS curves have been convolved with broad-

† The reasons for choosing AlNi are technical. They include the desire for a metallic material containing Al so that the KLV Auger spectra were accessible, simple crystal structure to facilitate electronic structure calculations, availability of XES spectra, and the absence of strong plasmon losses.

‡ This was a central conclusion of an international workshop on Unoccupied Electronic States, ICTP, Trieste [18].

§ We consider the self-energy to be the difference between the excitation energies of a quasi-particle calculation appropriate to the experiment in question and the calculated one particle eigenenergies. We neglect the modification of ground-state exchange correlation effects to dynamical effects in the excited state. The self-energy for Auger or XAS experiments includes the core hole potential. However, we separate the core hole effect from the electron–electron interaction, which dominates the self-energy effects in photoemission and Bremsstrahlung isochromatic spectroscopy (BIS).

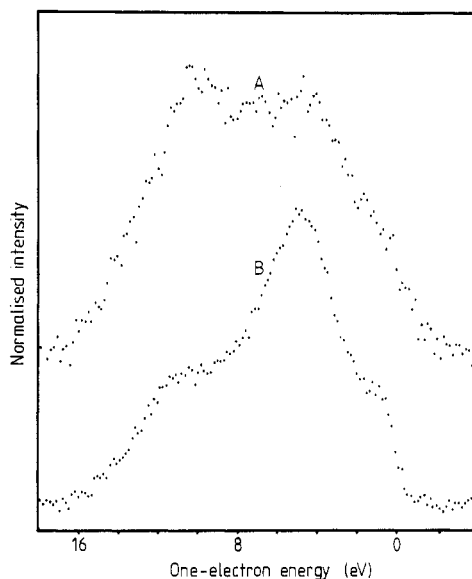


Figure 1. Auger spectra of AlNi: points A, KL_1V ; points B, $KL_{2,3}V$. Backgrounds have been subtracted from the data to make the heights above and below the peaks equal.

ening functions. For all spectra a Lorentzian broadening was applied to allow for the appropriate totals of Al K, L_1 , and/or $L_{2,3}$ lifetime widths (0.42, 0.73 and 0.004, respectively [25]). In addition we applied an energy-dependent lifetime broadening of $0.12(E - E_F)$ above the Fermi level E_F and $0.25(E_F - E)$ below E_F in order to allow for the finite lifetime of the valence-band excitations[†]. We also applied a Gaussian broadening of 0.5 eV (FWHM) for KV and KLV Auger spectra and 0.3 eV (FWHM) for LV x-ray emission spectra to account for the instrumental broadening. The KLV Auger spectra have been manipulated to reflect the s and p DOS and this merits further discussion. The raw data are given in figure 1. The x axis is the one-electron binding energy (E_b) of a valence electron in the presence of an L_1 or $L_{2,3}$ core hole. It is given by $E_b(K) - E_b(L) - E_k$, where E_k is the Auger electron kinetic energy. The KL_1V and $KL_{2,3}V$ spectra have different shapes because the angular parts of the matrix elements introduce a factor 3:1 in the s:p intensity ratio for KL_1V and 1:3 in $KL_{2,3}V$ [19–23]. The different shapes, combined with the knowledge of the angular parts of the matrix elements, allows us to assign the feature at about 9.9 eV to a peak of Al s symmetry, and the peak at about 5.0 eV to a peak of Al p symmetry.

Exact subtraction of the spectra to isolate the s and p state contribution is impossible because the radial parts of the matrix elements are not known, but a rough procedure was adopted which used the calculated impurity DOS as a guideline to improve the accuracy of the peak positions. The calculated Al* p DOS (figure 2) shows no shoulder below the peak at about 3.7 eV, so we subtracted sufficient KL_1V intensity from the $KL_{2,3}V$ spectrum to minimise the high binding energy shoulder (before subtraction, the $KL_{2,3}V$ was broadened with an extra Lorentzian broadening of 0.72 eV, because of the bigger lifetime broadening present in the KL_1V spectrum). The result is plotted top left in figure 2. For the s contribution to KL_1V , plotted in figure 3, sufficient $KL_{2,3}V$ intensity was subtracted from the KL_1V to obtain the best resemblance to the shape of the calculated Al* s DOS curve. These subtraction procedures are principally designed to increase the accuracy of the quoted peak positions in table 1. We think that the potential

[†] Few calculations of the lifetime of valence band excitation are available and none are directly appropriate to AlNi. The values we used are similar to those we have used elsewhere. (See e.g. [13, 26].)

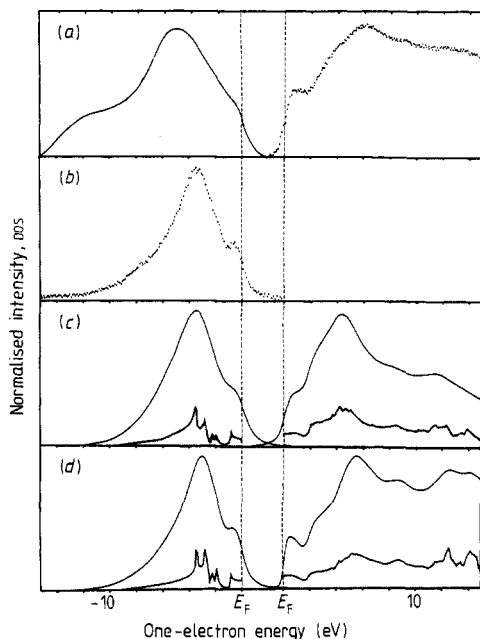


Figure 2. (a) Full curve, the Al p DOS in AlNi: resulting from the Al KLV Auger subtraction procedure (see text); points, the Al 1s XAS spectrum of AlNi: these reflect the Al p DOS in the presence of a core hole. (b) The KV XES reflects the Al p DOS in the absence of a core hole. (c) and (d) show computed Al p state densities and the broadened data as described in the text; (c) Al* p in AlNi; (d) Al p in AlNi. Al* denotes local DOS in the presence of a core hole. The Al* p DOS below E_F has been convolved with an extra Lorentzian of 0.7 eV to make comparison with the p from Al KLV Auger possible (see text). The data have been normalised to give the same peak height above and below E_F .

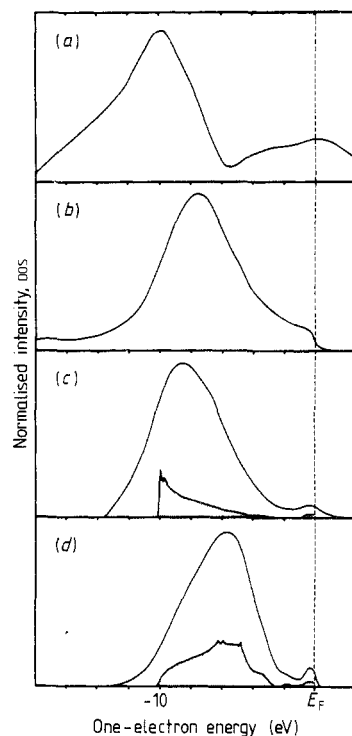


Figure 3. (a) Al s DOS in AlNi in the presence of a core hole obtained from subtraction procedures of Al KLV Auger spectra of AlNi (see text). (b) The Al LV XES spectrum, which closely reflects the Al s DOS in the absence of a core hole. (c) Computed Al* s and (d) computed Al s state densities below E_F , with the broadening as described in the text. The shaded areas show the unbroadened s DOS.

errors are <500 meV for the s peak position and <250 meV for the p peak. We do not recommend reliance on the detailed shapes of either the s- or the p-curves derived from Auger spectra in figures 2 and 3. Errors also occur due to uncertainties in broadening of asymmetric peaks in the DOS curves, particularly for the Al* s states in AlNi. However, once experimental and core-hole lifetime broadening has been taken into account, the peak does not shift by more than about 300 meV on further broadening.

The theoretical partial DOS curves for Al s and p states are presented in figures 3(c) and (d) and 2(c) and 2(d), respectively. For comparison with experiment, the calculated, raw data have been first cut off at E_F , then broadened as described above, and finally arbitrarily normalised to give the same peak height above and below E_F . The Al p states in AlNi show a large peak in the theoretical DOS at about 2.8 eV below E_F , which arises

Table 1. Summary of theoretical and experimental values for peak positions, shifts induced by core holes, and the self energies, Σ (all values in eV).

State	Theory	Experiment	(Method)	Σ
Al p	-2.8	-3.6	(XES)	0.8
Al* p	-3.7	-4.8	(AES)	1.1
core shift	0.9	1.2		
Al p	5.6			
Al* p	4.5	6.0	(XAS)	1.5
core shift	1.1			
Al s	-5.7	-7.4	(XES)	1.7
Al* s	-8.6	-10.0	(AES)	1.4
core shift	2.9	2.6		

from interaction with the Ni d bands [27] and represents bonding Ni d–Al p states. The Al s states (figure 3) are more nearly filled in Al alloys and are centred deeper in the valence-band than the Al p states. The tendency for the Al s states to pile up below the transition metal (TM) d bands is found in all AlTM alloys [27–30] and is not peculiar to AlNi. Above the Fermi level the Al p-DOS becomes broader and more free-electron-like.

The calculations for ‘core-ionised’ Al(Si) in AlNi show definite changes in the local DOS with respect to ‘neutral’ Al in AlNi. All the peaks are calculated to be more strongly bound. The calculated core-hole effects are larger for the s states than for the p states, which is related to the difference in spatial extension of these states and the resulting effective screening of the Coulomb attraction. This behaviour is well documented both experimentally and theoretically for the occupied states of Na, Mg, Al, and Si [19–23]. Thus the s-peak in figure 3 shifts by about 2.9 eV while the occupied p peak shifts by only about 0.9 eV in figure 2. Note also a shift of about 1.1 eV in the unoccupied Al p-state DOS when a core hole is introduced (see table 1). The fact that the redistribution of states around the perturbed site is similar for the compound and pure element is due to the screening being well localised within the Wigner–Seitz sphere and in this way mainly determined by the local DOS of the ‘neutral’ site.

The upper halves of figures 2 and 3 show experimental data. The Al K and Al L_{2,3} XES spectral shapes are dominated by the Al p- and s-DOS distributions, respectively [4]. The experimental shapes of the XES spectra closely reflect the calculated partial DOS in figures 2 and 3. Inclusion of the single-particle, matrix-element effects would presumably improve the agreement still further [31]. However the peak energies are shifted by 0.8 eV for Al K XES and 1.7 eV for Al L_{2,3} XES (see table 1). We attribute these discrepancies between experiment and the single-particle calculation to self-energy effects [12–17, 28]. The discrepancies are greater than those found for simple metals but it is well known that self-energy effects are large in Ni and its compounds ([32] and references therein).

The peak positions for the s- and p-contributions to the Auger spectra are best derived from the curves in figures 2 and 3. The differences compared with the XES positions, given in table 1, represent an experimental measure of the influence of the core-hole potential. Values of 2.6 and 1.2 eV for s- and p-peaks, respectively, may be compared directly with the theoretical values of 2.9 and 0.9 eV. The agreement is, in our opinion, good. This supports, *a posteriori*, our use of a single impurity atom calculation

(equivalent core approximation) to treat the different core levels involved (2s in KL_1V and 2p in $KL_{2,3}V$). We may conclude that the calculations give a reliable estimate of the core hole effects, and that these are larger for the Al s-states at the bottom of the band, than for the p-state peak. For the unoccupied states we have no site-selective information on the Al states above E_F from experiments where no core hole is present. We have measured the high energy inverse photo-emission (BIS) spectrum (not shown) which has no core hole effect, but the features are dominated by the Ni states and therefore bear little resemblance to the unoccupied Al DOS [33, 34]. Thus, no direct experimental evidence is available for the influence of the core hole potential in XAS of Al in AlNi. However, the success of the computations for the shifts induced in the occupied states also allows us to place trust in the computations for the unoccupied states. The calculated shift of the p-state peak about 6 eV above E_F is approximately 1.5 eV. Such a shift is significant. It indicates the need for extreme caution in the use of XAS when extracting information on the one-particle excitations in the presence of a core hole for atoms like Al in alloys and compounds. Similar caution is required when trying to compare XAS data with other spectra in order to see whether states centred on different sites are mixed.

Finally, we remark that the effects of the attractive core-hole potential on the p bands are more pronounced for the unoccupied state than for the occupied states. This may well be due to the different widths of the occupied and unoccupied parts of the p bands and therefore to the different phase space available for the spectral redistribution driven by the core-hole potential. (In particular, note that most of the detailed structures in the raw DOS do not shift in energy, but just vary in intensity.)

In summary, we have shown by a combination of various types of high-energy spectroscopies and DOS calculations that core-hole effects are not negligible in either occupied or unoccupied Al-derived states in AlNi. We have also shown, by comparison of DOS calculations and experimental data, that self-energy effects for electron-electron interaction and core-hole effects are of the same order of magnitude in AlNi. This demonstrates that a simple comparison of, for instance, XAS and a DOS calculation, is not a reliable guide as to whether or not core-hole effects are important.

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References

- [1] Parratt L G 1959 *Rev. Mod. Phys.* **31** 616
- [2] Fabian D J, Watson L M and Marshall C W 1972 *Rep. Prog. Mod. Phys.* **34** 601
- [3] Hedin L 1974 *X-ray Spectroscopy* ed. L V Azaroff (New York: McGraw-Hill) p 226ff
- [4] von Barth U and Grossman G 1982 *Phys. Rev. B* **25** 5150
- [5] Kotani A and Toyozawa Y 1979 *Synchrotron Radiation* ed. C Kunz (Berlin: Springer) p 169
- [6] Dehmekhin V F 1974 *Fiz. Tverd. Tela* **16** 1020 (English translation *Sov. Phys.—Solid State* **16** 659)
- [7] Bonnelle C, Karnatak R C and Sugar J 1974 *Phys. Rev. A* **9** 1920

- [8] Thole B T, van der Laan G, Fuggle J C, Sawatzky G A, Karnatak R C and Esteva J-M 1985 *Phys. Rev. B* **32** 5107
- [9] Fink J, Müller-Heinzerling Th, Scheerer B, Speier W, Hillebrecht F U, Fuggle J C, Zaanen J and Sawatzky G A 1985 *Phys. Rev. B* **32** 4899
- [10] Zaanen J, Sawatzky G A, Fink J, Speier W and Fuggle J C 1985 *Phys. Rev. B* **32** 4905
- [11] Waddington W G, Rez P, Grant I P and Humphreys C J 1986 *Phys. Rev. B* **34** 1467
Waddington W G, Rez P, Grant I P and Humphreys C J 1987 *Phys. Rev. B* **35** 5297
- [12] Hedin L 1965 *Phys. Rev. A* **139** 796
Hedin L and Lundqvist S 1969 *Solid State Phys.* **23** 1
- [13] Nilson P O and Larsson C G 1983 *Phys. Rev. B* **27** 6143
Speier W, Zeller R and Fuggle J C 1985 *Phys. Rev. B* **32** 3597
- [14] Jackson W B and Allen J W 1988 *Phys. Rev. B* **37** 4618
- [15] Shung K W-K, Sernelius Bo E and Mahan G D 1988 *Phys. Rev. B* **36** 4499
Northrup J E, Hybertsen M S and Louie S Q 1987 *Phys. Rev. Lett.* **59** 819
- [16] Godby R W, Schlüter M and Sham L J 1986 *Phys. Rev. Lett.* **56** 2415
- [17] Horsch P, von der Linden W and Lukas W D 1987 *Solid State Commun.* **62** 359
- [18] *Proc. Int. Workshop on Unoccupied Electronic States (ICTP, Trieste) 1988*
- [19] Lässer R and Fuggle J C 1980 *Phys. Rev. B* **22** 2637
- [20] Fuggle J C 1981 *Electron Spectroscopy IV* ed. C R Brundle and A D Baker (London: Academic) p 85
- [21] Weightman P, Davies M and Inglesfield J E 1986 *Phys. Rev. B* **34** 6843
- [22] Hannah P H, Weightman P and Andrews P T 1985 *Phys. Rev. B* **31** 6238
Davies M and Weightman P 1984 *Phys. Rev. B* **30** 4183
Davies M and Weightman P 1985 *Phys. Rev. B* **32** 8423
- [23] Ramaker D E, Hutson F L, Turner N H and Mei W N 1986 *Phys. Rev. B* **33** 2574
- [24] Zeller R 1988 *Z. Phys.* **72** 79
- [25] Krause M O and Oliver J H 1979 *J. Phys. Chem. Ref. Data* **8** 329
- [26] van der Marel D, Sawatzky G A, Zeller R, Hillebrecht F U and Fuggle J C 1984 *Solid State Commun.* **50** 47
- [27] Watson L M and Kapoor P 1972 *Proc. Int. Symp. X-ray Spectroscopy and Electronic Structure of Matter* vol. 2 ed. A Faessler and G Wiech (München: Fotodruck Frank) p 135
- [28] Fuggle J C, Hillebrecht F U, Zeller R, Zolnierok Z, Bennett P A and Freiburg Ch 1982 *Phys. Rev. B* **27** 2145
- [29] Fuggle J C, Watson L M, Fabian D J and Norris P R 1973 *Solid State Commun.* **13** 507
- [30] Fuggle J C, Källne E, Watson L M and Fabian D J 1977 *Phys. Rev. B* **16** 750
- [31] Schwartz K, Neckel A and Nordgren J 1979 *J. Phys. F: Met. Phys.* **9** 2509
- [32] Fuggle J C, Sawatzky G A and Allen J W (ed.) 1988 *Narrow Band Phenomena* (New York: Plenum) p 145
- [33] Speier W, Fuggle J C, Durham P, Blake R, Sterne P and Zeller R 1988 *J. Phys. C: Solid State Phys.* **21** 2612
- [34] Sarma D D, Speier W, Zeller R, van Leuken E, de Groot R and Fuggle J C 1989 *J. Phys.: Condens. Matter* at press