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Electronic structure of Al_3Ni and $AlNi_3$ alloys

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Experimental Al $KL_{23}V$ and Ni LMM Auger and high-resolution valence band XPS spectra of Al_3Ni and $AlNi_3$ alloys are presented and compared to the corresponding spectra of pure metals. The spectra are interpreted in terms of the results of the discrete-variational (DV)-$X\alpha$ cluster MO model using atomic Auger transition probabilities. Good agreement has been obtained between the theory and experiment concerning the energy widths of the spectra. For Al_3Ni the total number of electrons at the Fermi level obtained from the calculations agrees better with the experimental value than those from previous calculations. In the case of the alloys, the calculated charge transfer is small (<0.4 electrons), playing only a minor role in the filling of the Ni *d* band. The hybridization between the Ni *d* and Al *s* and *p* bands can be deduced from the reduction of the Al *s and p* DOS at the Ni *d* resonance energy. Our results suggest that for these alloys the corresponding Auger matrix elements do not depend on the Auger transition energy. The Ni LMM spectra of the alloys demonstrate the localization of the Ni *d* band. [S0163-1829(96)04735-2]

INTRODUCTION

Studies of the effect of changes in the local electronic environment on atomic processes in components of alloys can make a valuable contribution to the understanding of electronic properties of these materials. For theories of alloy stability, the charge transfer is of special interest. Particularly interesting are the cases of the simple metal–transition metal (TM) alloys, where a significant contribution to the filling of the *d* bands of the transition metal can come from hybridization and from charge transfer.[1,2] Effects of alloying can be observed clearly in dilute alloys, where an atom of one metal can be almost entirely surrounded by atoms of the other constituent. Ni is an interesting transition-metal component in such alloys because it is possible to change the Ni *d* band filling by alloying such that the number of unfilled states becomes zero. To study the hybridization between the *d* orbitals of the TM and the *s and p* orbitals of the simple metal. Al is a good metal partner component, because, as in the case of $MgNi_2$,[2] the expected hybridization effects are strong. The studies of the electronic structure of Al-Ni alloys allow us to obtain relevant information like the applicability of the final state rule[3] for the interpretation of the Al core-valence Auger line shapes, and the effect of the transition energy dependence of the Auger matrix elements on Al K Auger spectra.[4]

The purpose of this paper is to present experimental Al $KL_{23}V$, Ni LMM Auger and x-ray photoelectron spectra of Al_3Ni and $AlNi_3$ alloy samples and to interpret the experimental spectra using a cluster-type molecular orbital model. From the core-valence Auger spectra, information can be obtained on the site-projected local density of electron states as well as on the role of the different excitation processes. The measured alloy and metal[4] Al $KL_{23}V$ Auger spectral shapes are compared to each other and with the theoretical

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spectra derived from the cluster DV-$X\alpha$ model calculations. The calculated spectral shapes approximate well the width of the experimental spectra and indicate that the energy dependence of the Auger matrix element correction is almost negligible for the Al $KL_{23}V$ spectra. Comparing the Ni L_3VV spectra of pure Ni and the two alloys, considerable differences can be observed in the respective satellite structures. The calculations also allow us to estimate the value of the charge transfer in these alloys.

EXPERIMENT

Al $KL_{23}V$ Auger spectra of $AlNi_3$ and Al_3Ni polycrystalline alloy samples, excited by Mo x rays, were measured with a home built, high luminosity electron spectrometer (ESA-31).[5] The spectrometer, based on a 180° hemispherical analyzer, was used in the fixed retardation ratio (FRR) working mode. The energy resolution was 0.4 eV in the case of the Al KLV spectra. During the measurements the vacuum was better than 10^{-7} Pa in the chamber and the sample surface was cleaned by applying successive Ar^+ ion sputtering. The negligible level of oxidation of sample surfaces was monitored by measuring the Al KLL Auger electron spectra. Valence-band XPS spectra were measured using a SCIENTA ESCA-300 system equipped with a rotating anode (Al $K\alpha$) radiation source, an x-ray monochromator, and a hemispherical analyzer.[6] The energy resolution of the spectrometer was 0.4 eV, the sample surface was cleaned by ion sputtering. Energy calibration of electron spectra presented here was performed with the aid of the photoelectron and Auger electron lines from polycrystalline Cu and Ag samples.[7]

DV-$X\alpha$ CALCULATIONS

Calculations were performed using the cluster type DV-$X\alpha$ approximation for non-spin-polarized electrons developed by Adachi *et al.*[8] All the calculations of density of states and charge distribution were performed using experimental lattice constants.[9,10] The $AlNi_3$ alloy is a cubic-ordered (O_h) intermetallic compound which crystallizes in the Cu_3Au structure, the three Ni atoms occupying the face centers and the Al atoms the cube corners. Al_3Ni has a complicated orthorhombic (DO_{20}) structure. Tables I and II contain the positions of atoms in atomic units for the two alloys. For these compounds we used the sphere radii of the constituent atoms given by Slater.[11] The values of the sphere radii influence the determination of the charge transfer inside the cluster. To describe the valence states, the outermost orbitals involved in the calculations were chosen to be ($3d$) for Al atoms and ($4p$) for Ni atoms. The exchange parameter α in the DV-$X\alpha$ model was constant, $\alpha=0.7$ suitable[12,13] for transitional metal compounds. For the numerical iteration the self-consistent-charge scheme[14] was used. To get realistic binding energies for the valence states involved, transition-state calculations[11] were performed. The density of states (DOS) profile is given by replacing each discrete level by a Lorentzian with a width of 0.8 eV,[8] weighted by the degeneracy of the orbitals. In the case of $KL_{23}V$ Auger transitions we have an additional broadening of 0.9 eV which consists of the sum of width of Al $1s$ level (0.38 eV),[15] and the Al $2p$ level (0.012 eV),[15] the contribution from the finite energy resolution (0.4 eV), and from the phonon broadening [0.11 eV at 300 K (Ref. 16)]. For obtaining the theoretical XPS spectra, the atomic components of the DOS have been weighted by the corresponding photoionization cross sections of Scofield.[17] In the cluster type DV-$X\alpha$ calculation we have 16 atoms for the Al_3Ni cluster and 14 atoms for the $AlNi_3$ cluster. It is difficult to increase the number of atoms especially in the case of Al_3Ni cluster due to the orthorhombic structure. The calculated Al $KL_{2,3}V$ Auger line shapes have been obtained using the DV-$X\alpha$ method and the final state rule with the following assumptions: (i) the line shape is determined by the final state LDOS with the presence of the L_{23} final state core hole, (ii) for the ratio of the Auger matrix element the value in the case of Al metal is taken from the atomic value as $KL_{23}s/KL_{23}p=0.25$.[23]

TABLE I. The position of atoms in the Al_3Ni cluster (Refs. 10 and 26) in atomic units.

Atom	*x*	*y*	*z*
Ni	0.000	0.000	0.000
Ni	3.273	6.931	8.092
Ni	6.246	0.000	3.546
Ni	9.520	6.931	4.546
Al-1	1.499	6.931	3.273
Al-1	1.774	0.000	4.819
Al-1	7.746	6.931	0.272
Al-1	8.021	0.000	7.819
Al-2	3.810	2.731	0.809
Al-2	3.810	11.132	0.809
Al-2	5.709	4.200	5.355
Al-2	5.709	9.663	5.355
Al-2	10.057	2.731	2.736
Al-2	10.057	11.132	2.736
Al-2	11.956	4.200	7.283
Al-2	11.956	9.663	7.283

RESULTS AND DISCUSSION

In Fig. 1 the shapes of the XPS valence-band spectra of Al_3Ni and $AlNi_3$ alloys are shown. As it has been pointed out earlier,[1,24] with increasing dilution of nickel in aluminum, the nickel $3d$ bands, which dominate the spectra, become narrower and pull away from the Fermi level. At the same time, the d^9 correlation satellites disappear, due to the filling of the nickel $3d$ band[25] and the bottom of the Al *s and p* band is superimposed to the satellite region. A difference can be seen, however, between the previous experiment[24] and ours in the case of the Al_3Ni alloy, regarding the position of the shoulder near the Fermi level.

Figures 1(a) and 1(b) show the theoretical XPS spectra

TABLE II. The position of atoms in the $AlNi_3$ cluster (Ref. 9) in atomic units.

Atom	*x*	*y*	*z*
Ni	0.000	3.3712	0.000
Al	3.3712	3.3712	3.3712

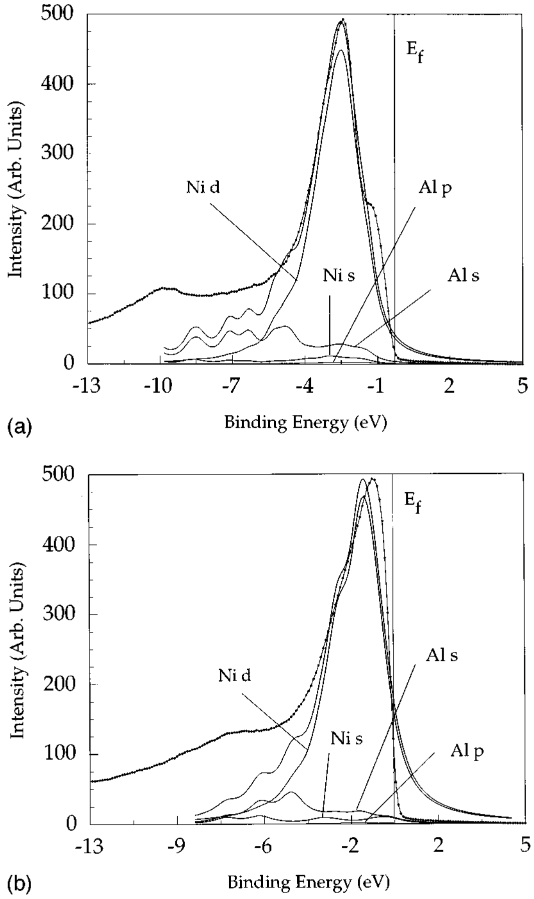

FIG. 1. Comparison of the measured and calculated valence band XPS spectra. (a) Al_3Ni, (b) $AlNi_3$.

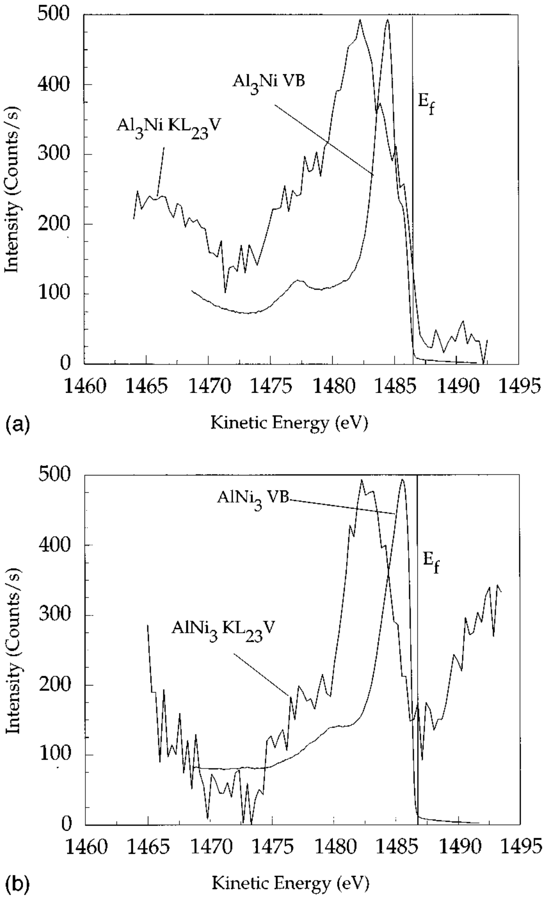

FIG. 2. Comparison of the measured Al $KL_{2,3}V$ Auger spectra and valence-band XPS spectra. (a) Al_3Ni, (b) $AlNi_3$.

obtained from our DV-$X\alpha$ calculations in comparison with the measured spectra. The agreement between the theoretical and experimental spectral shapes is satisfactory regarding the bandwidths. Appearing at around -9 eV in the spectra, the correlation ''shake-up'' d^8 satellite is created in the Ni photoemission process in an intrinsic way. While in the case of Al_3Ni the calculation predicts the energy position of the maximum correctly, in agreement with the experiment and with recent band-structure calculations[26] [the $3d$ (t_{2g}) peak is at the same position, namely -2.9 eV], for $AlNi_3$ this maximum is shifted by ~ 0.5 eV towards higher binding energy relative to the maximum in the experimental spectrum. The spectra are dominated by the Ni d contributions, however, in different ratios for the two alloys. The Al s contributions show maxima at the bottom of the valence band. To test our calculations we compared the total DOS at E_f obtained from the DV-$X\alpha$ model, with that obtained from specific-heat measurements. For Al_3Ni the experimental total number of electrons (in Ry^{-1} per cell) is 28.6,[27,28] and from our calculations we have 30.02. This latter value is in a better agreement with the experiment[28] than those obtained from earlier calculations. Based on the saturation magnetic moment[29,30] it is generally agreed that the d band of Ni contains about 9.4 electrons. A population analysis of the DV-$X\alpha$ results indicates that the number of d electrons is only 8.74 in the case of the $AlNi_3$ alloy and 8.73 in the case of the Al_3Ni alloy. These results suggest that there must be some d character in the unoccupied sp states of Ni. The hybridization strength, due to the proximity in energy of the Al p and Ni d bands, is very strong.[31]

Figures 2 and 3 show the experimental Al $KL_{2,3}V$ Auger spectra of the alloys in comparison with the XPS valence-band spectra and with the $KL_{23}V$ Auger spectrum of metallic Al.[32] The energy scales of the Auger spectra shown in the figures correspond to the binding energy of single-particle densities of states:

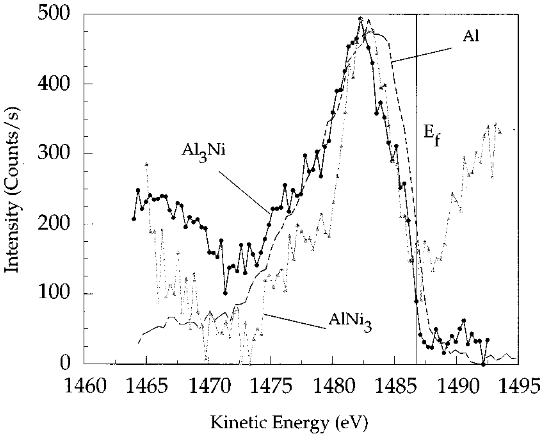

FIG. 3. Comparison of the Al $KL_{2,3}V$ Auger spectra of Al_3Ni, $AlNi_3$, and Al (Ref. 32).

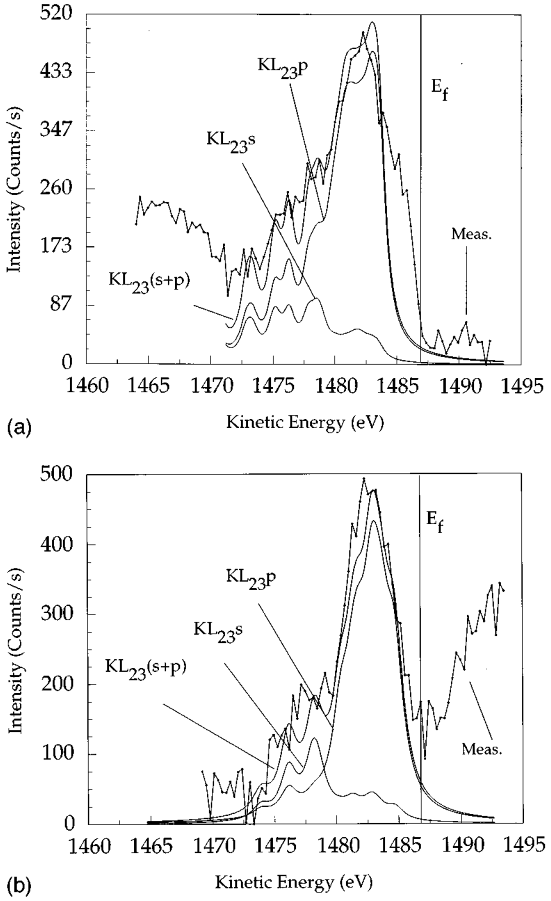

FIG. 4. Theoretical Al $KL_{23}V$ in comparison with the measured spectra. (a) Al_3Ni; (b) $AlNi_3$.

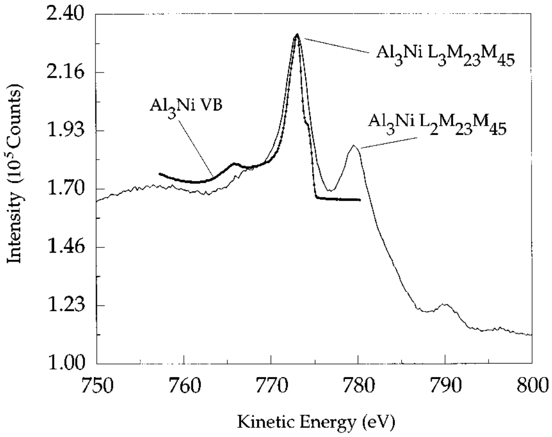

FIG. 5. The measured Ni $L_3M_{2,3}M_{45}$ Auger spectra of Al_3Ni, in comparison with the corresponding valence-band XPS spectrum.

$$E_B^F(V)=E_B^F(K)-E_B^F(L_{23})-E_{\mathrm{kin}}^F(KL_{23}V),$$

where the core binding energies $E_B^F(K)$, $E_B^F(L_{23})$, and the Auger kinetic energy E_{kin}^F are referenced to the Fermi level, assuming that the Coulomb repulsion between the two final state holes is negligible.[3] The deviation of the Al $KL_{2,3}V$ profiles from the spectral shape of the valence-band photoelectron spectra (Fig. 2) can be attributed to the influence of the core hole on the ionized Al atoms or local DOS (LDOS) as expected.[18,33,34] This view is supported by the similarity in shape of the Al $KL_{23}V$ spectra in the alloys and in pure Al metal (Fig. 3).[32] In spite of the large difference in the concentration of Ni (0–75 %), the overall width of the spectrum in both alloys is close to that of metallic Al (Fig. 3). The studies of Mg KLV spectra in a range of alloys and their interpretation in term of the final state rule[18] lead us to expect that the shoulder on the high kinetic energy edge of the Al KLV spectrum in the alloys arises from hybridization of the local p DOS on an Al site with the Ni d band. The narrowing of the intense central peak in the Auger electron spectrum of $AlNi_3$ is expected to arise from the narrowing of the p DOS in a more dilute alloy.[25] This narrowing makes it possible to observe the distorted s PDOS in the core ionized Al. Figures 2 and 3 confirm that if the Ni d DOS is concentrated near E_f then this region will have a reduced Al DOS at the Fermi energy due to the Ni d–Al s,p hybridization.

Figure 4 shows the theoretical Al $KL_{23}V$ spectra in comparison with the measured spectra. In Al metal the $KL_{2,3}V$ spectral shape is dominated by the p density of states[32] around a site with a core hole. The soft-x-ray KV spectra of Al metal[3] exhibit the spectral profile of the p LDOS around a neutral atom. From the comparison of these spectra it can be concluded that the influence of the initial core hole on the local p DOS and hence on the $KL_{2,3}V$ Auger line shape is almost negligible.[3] In the case of Al_3Ni and $AlNi_3$ alloys the Al p/s ratios of the contributions to the $KL_{2,3}V$ spectra are 3.4 and 3.9, respectively. In a simple metal–transition-metal alloy the simple metal KLV spectrum can provide insight into the electron-electron interaction between the simple metal band and transition-metal d band. In our case the shape of $KL_{2,3}V$ Auger transition in the alloys Al_3Ni and $AlNi_3$ is very similar, which can be understood in terms of a weak electron-electron interaction so that the one-electron spectrum calculated in the $X\alpha$ approximation coincides with the experimental spectrum.[35] Comparing the measured Al $KL_{2,3}V$ Auger spectra of the alloys and the pure aluminum[32] a small energy shift of the spectra can be found (Fig. 3) in the case of the Al_3Ni and $AlNi_3$ alloys, relative to the Al metal. The reason for this energy shift is the reduction of the Al DOS at the Ni d energy position due to hybridization effects. Comparing the theoretical Al $KL_{23}V$ Auger spectra obtained for alloys to that obtained for the metallic Al,[32] one can observe a difference in the energy distribution of the s PDOS, which is pulled away from the Fermi level with increasing Al content. In the case of $AlNi_3$ the calculated line shape agrees well with the experimental one [Fig. 4(b)] predicting correctly the position of the maximum and the width of the energy distribution, the energy position and the relative intensity of the contributions appearing due to the s PDOS, and the slight decrease in the p PDOS as a consequence of the Ni d–Al p hybridization. These contributions cause shoulders at the low and high kinetic energy part of the spectrum. For Al_3Ni [Fig. 4(a)] the calculation describes the position of the maximum and the position of the shoulder due to the s PDOS quite well; however, it cannot account for the appearance of the shoulder at the higher kinetic energy side and gives a somewhat lower energy width (FWHM). From the spectra shown in Fig. 4 it can be concluded that the energy corrections of the KLV Auger matrix elements are negligible, contrary to the case of Mg alloys.[4,2] The Ni $L_3M_{23}M_{45}$ spectrum is compared with the valence-band XPS spectrum in Fig. 5 in the case of the Al_3Ni alloy. Detailed calculations[36] show that this component of $L_3M_{23}M_{45}$ Auger spectrum consists of two terms of the multiplet structure which are about 1 eV apart and have an intensity ratio of $\simeq$5:1. The inclusion of a weaker component would improve the agreement between the shape of the XPS valence band and $L_3M_{23}M_{45}$ line shape which, as Fig. 5 illustrates, is already good. The similarity of the spectrum shapes again confirms that in the sites of Ni core ionized atoms the LDOS is very different from that in the core ionized Al sites and is dominated by the strongly localized Ni $3d$ band.

SUMMARY

Using DV-$X\alpha$ cluster model for interpretation of the high-resolution XPS valence-band spectra of $AlNi_3$ and Al_3Ni polycrystalline alloy samples and performing the calculations in the case of Al_3Ni with the realistic DO_{20} orthorhombic structure, a satisfactory agreement has been obtained with the experimental spectral shape. For Al_3Ni the total number of electrons around the Fermi level obtained from our calculations (30.02 Ry^{-1} per cell) is in a better agreement with the experimental value (28.6 Ry^{-1} per cell) than the theoretical value reported earlier.[28] The charge transferred from the Al *s and p* orbitals to the Ni *d* band is 0.34 and 0.2 electrons from our calculation for Al_3Ni and $AlNi_3$, showing that the charge transfer plays only a minor role in the filling of the Ni $3d$ band. In both alloys the Al $KL_{23}V$ Auger spectral shape, dominated by the *p* partial DOS, is determined by the local DOS around the core ionized Al atoms, differing from the local DOS at Ni sites. Evidence for the hybridization is coming from the details of the experimental spectral shapes. The appearance of a shoulder at the high kinetic energy edge and energy shift of this edge relative to the spectrum of pure Al metal are attributable to the reduction of the Al *s* and *p* DOS at the Ni *d* peak energy. Our cluster MO interpretation gives correct predictions for the spectral widths and indicates that corrections for energy dependence of the Auger matrix elements[4] can be neglected in the case of the Al $KL_{23}V$ spectra in these alloys. The localization of the Ni bands in Al_3Ni is demonstrated by the similarity between the shapes of the Ni $L_3M_{23}M_{45}$ and XPS valence-band spectra and is leading to suppression of the Al plasmon satellites with increasing Ni concentration in the measured Ni LMM spectra.

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