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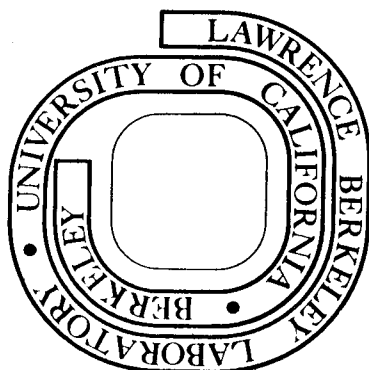
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AN X-RAY PHOTOEMISSION INVESTIGATION
OF THE DENSITY OF STATES OF β' -NiAl*

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ABSTRACT

The electronic structure of β' -NiAl was studied by x-ray photoemission spectroscopy (XPS). The observed valence band density of states agrees quite well with the non-relativistic APW calculations of Connolly and Johnson. These results are also compared with other experimental data. The hypothesis of d-band filling is supported by our XPS measurements.

Our knowledge of the electronic structure of alloys is still in a rudimentary stage. Even for simple alloys, relatively sophisticated band-structure calculations have been undertaken only in the past decade. Experimental techniques for characterizing alloy band structure are also still evolving. Consequently there are still many unanswered questions about the electronic properties of alloys. In this paper we report the use of x-ray photoemission spectroscopy (XPS) to address one such question: the filling of the nickel d-bands in β' -NiAl.

According to the theory of alloys developed along the lines suggested by Engel and further developed by Brewer, nickel should have a $3d^{10}$ configuration in NiAl.¹ This follows because the crystal structure of an alloy system can be correlated with the total number of s and p valence electrons per unit cell. The bcc crystal structure occurs for a concentration of three or fewer s and p electrons per unit cell (i.e., 1.5 electrons per atom), which implies a net donation of electrons for the filling of the Ni d-bands. More sophisticated theories essentially support this point of view. Connolly and Johnson carried out a non-relativistic APW calculation on NiAl which showed nearly all of the nickel d-band falling below the Fermi energy (E_F).² They gave a detailed density of states which facilitates comparison with experiment.

The experimental techniques that bear on this question are those which probe the total valence-band density of states (VB DOS), such as XPS. While relatively few alloy systems have been studied by XPS, the close connection between XPS spectra and the VB DOS in metals and semiconductors indicates that this method should yield the initial-state

density with some reliability. In addition Ni core-level spectra might be expected to show differences both in structure and in binding energy depending on whether or not the Ni d-band is filled. In this paper we report a high-resolution XPS study of β' -NiAl.

NiAl is a member of the class of alloys which form β' phase alloys at approximately a 50-50 atomic percent composition. These alloys have the B2 (CsCl) crystal structure and are ordered at room temperature. For the NiAl system, the B2 phase occurs between 40 and 55 atomic percent of Al.^{2,4} The samples used in the experiments were prepared by melting stoichiometric amounts of high-purity Al and Ni (99.999% for each) in an argon arc furnace with a water-cooled copper hearth. The resulting button was then remelted four times. After each melting, the weight loss was checked. The total weight loss never exceeded 0.4%. The crystal structure was checked by x-ray diffraction, which showed that only the β' phase was present.

It is well known that XPS is very surface-sensitive; thus extreme caution must be taken to prepare clean samples. Standard sample preparation methods include evaporation, ion bombardment, or heat treatment. These techniques, which work well for elemental metals, are not very applicable for alloys, because they could easily produce a change of composition or phase within the XPS sampling depth (~ 20 Å). Thus, to prepare suitable samples one must either cleave (fracture) or mechanically clean the sample in situ. For the β' -NiAl alloy, the latter method was chosen. A device was fabricated which had linear and rotary motion and on which either a tungsten wire brush or a tungsten carbide milling tool could be attached on the vacuum side.^{3a}

After the sample was mechanically cleaned by in situ scraping in the sample preparation chamber (pressure $< 2 \times 10^{-9}$ Torr), it was inserted directly into the main spectrometer vacuum ($< 5 \times 10^{-10}$ Torr).

The measurements were carried out in a modified Hewlett-Packard 5950A electron spectrometer with a total instrumental resolution of 0.55 eV. First 20 eV scans of the O 1s, C 1s, and W 4d regions; as well as an overall 0-1280 eV binding energy scan were made as in situ analyses for contamination. These scans were repeated after the valence region was studied. The valence band measurements required accumulation times of approximately 8 hours and were repeated three times on freshly prepared surfaces. The oxygen and carbon contamination amounted to less than 0.1 monolayer.

Figure 1 shows the XPS-VBDOS, corrected for inelastically scattered electrons, which was obtained for β' -NiAl. A smooth background contribution was subtracted under the assumption that each point in the spectrum contributes to the inelastic tail in proportion to its initial intensity. This corrected spectrum is compared with the calculated density of states of Connolly and Johnson² using the (non-relativistic) Augmented-Plane-Wave (APW) method in conjunction with an LCAO interpolation scheme. Table I compares theory and the XPS results along with ultraviolet photoemission spectroscopy (UPS) and x-ray data. A comparison between Fig. 1 and Fig. 2 reveals that the VBDOS is not a superposition of the VBDOS's of pure Al metal and pure Ni metal. The Al VBDOS^{3,6} is very nearly free-electron-like with a few very weak features, and because of its low intensity would only slightly distort the Ni metal VBDOS if it were superimposed.⁷ Secondly, the general shape of the valence-band spectrum agrees well with the calculated VBDOS of

Connolly and Johnson² and the more recent KKR results of Moruzzi, Williams, and Janak.⁸ The latter authors examined the effects of alloying on total band width by means of KKR calculations on a series of six (CsCl type) intermetallics. They found in general a band narrowing in these systems. This narrowing can result from either 1) a lack of d-density of final states on neighboring atoms onto which electron tunneling can occur or 2) mutual d-band repulsion. The latter is of course not operative in the NiAl case because only one of the components has d-bands. For β' -NiAl we obtain a band narrowing N^9 (relative to Ni metal) equal to 0.06 as opposed to 0.33 given by Moruzzi, et al.⁸ This comparison is not strictly valid because Moruzzi, et al. used a hypothetical diatomic Ni moiety as a reference and we are using Ni metal. It is also somewhat hazardous to determine the experimental d-band width from a Ni metal XPS VBDOS in which multi-electron effects appear to be important.^{3a} In the case of β -brass (CuZn) for which the last objection is not important, we obtain, using the recent results of Wertheim, et al.,¹⁰ a value $N = .11$ (relative to Zn metal) and $N = .13$ (relative to Cu metal) as opposed to .82 (relative to Zn_2) and .66 (relative to Cu_2) as given by Moruzzi, et al. The predicted values are again far from the observed values but β' -NiAl is predicted to have N about half as large as β -brass, as observed. Band-narrowing has also been reported in the Cd-Mg system.¹¹

By carrying their calculations to self-consistency, Moruzzi, et al.⁸ were able to compute charge densities and discuss charge transfer. Charge transfer in NiAl is related to the question of the occupancy of the d-bands. Several experimental results suggest that Al 3s electrons are transferred to Ni and fill or very nearly fill the d-band.¹²⁻¹⁴ This point is, however, subject to some controversy.¹⁵ Resolution of

the question of d-band filling might seem to be easily determined by measuring the "chemical shift" of β' -NiAl core lines with respect to the pure metals. However, as tabulated in Table II, there appears to be no shift in the Al lines and only small shifts in different directions for the various Ni lines. In general large shifts in metals have not been observed because of opposing effects - "charge transfer" versus relaxation.¹⁶ The implication of the Ni line positions is not clear because multiplet effects¹⁷ may cause shifts in the spectral weight. Wertheim, et al.¹⁰ observed a very small shift in CuZn, where no complications exist due to multiplet splitting. The Moruzzi, et al. calculations⁸ indicated a much larger charge transfer in β' -NiAl (compare their Figs. 7 and 9), which means a larger shift. However the filling of the d-band should greatly reduce the relaxation because of the loss of d-wave screening.¹⁶ This effect should be most pronounced in the Auger spectrum where there is a two-hole final-state; however very little relaxation shift is observed in the Ni LMM Auger lines (cf. Fig. 3).

Another effect of a filled d-shell would be the absence of the multiplet structure on the Ni core levels in β' -NiAl as opposed to Ni metal. The Ni 3s level is considerably more symmetric in β' -NiAl than in Ni metal and is significantly narrower (by 0.7 eV). The full-widths at half-maximum (FWHM) of the various levels in β' -NiAl and Ni and Al metals are tabulated in Table III. The Al levels are nearly the same in the alloy as in the metal, while all the Ni lines are considerably narrower. Next, consider the structure in the Ni 3p level. It is qualitatively similar in the alloy and Ni metal; however, the

splitting of the two components in β' -NiAl is 1.80 (05) eV as opposed to the 1.33 (10) eV splitting in Ni metal. We should compare these values with the observed spin-orbit splitting in the neighboring filled d-band metals, Cu (2.2 eV) and Zn (2.6 eV). Clearly the splitting in β' -NiAl is reasonable for spin-orbit splitting in a closed-shell Ni atom, whereas the Ni metal splitting is influenced by multiplet effects.

The 2p levels of Ni in paramagnetic compounds show intense satellites (with intensities as much as 50% that of the primary peak) at higher binding energy, while compounds with diamagnetic Ni and Cu metal, with a filled d-band, do not show this satellite structure.¹⁸ Ni metal itself exhibits readily observable satellites with approximately 10% the intensity of the primary peak. In β' -NiAl the 2p satellites are very weak or absent (Fig. 4). This observation again supports a filled d-band hypothesis in β' -NiAl.

In summary, the XPS spectrum of valence states in β' -NiAl is in good agreement with UPS measurements of Nilsson.⁴ The XPS results further support the interpretation of a filled Ni 3d band and afford further confidence in Connolly and Johnson's interpretation of the optical data¹⁹ in terms of transitions between the valence bands and conduction bands.

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Table I. Comparison of features in the VB DOS of β' -NiAl obtained by several techniques. (Energies in eV)

	A	B	C	D	E ^h
XPS ^a (β' -NiAl)	0.63(08)	1.84(08)	3.17(12)	4.54(12)	9.4(2)
APW ^b (β' -NiAl)	0.7	1.9	3.0	4.8	$\sim 11^b \sim 10^g$
UPS ^c (β' -NiAl)	0.8	2.1			
SXS-ALK β ^d (β' -NiAl)	0.7		3.3	5.5	11.7
SXS-NiL _{III} ^d (β' -NiAl)		1.8		4.8	
XPS-Al ^e (metal)	—	—	—	—	~ 10
XPS-Ni ^f (metal)	—	—	—	—	~ 8.9

^a This work^b Ref. 2^c Ref. 4^d Ref. 5^e Unpublished work, this laboratory^f Ref. 3^g Ref. 8^h Total bandwidth

Table II. Core-level binding energies (eV) for Ni metal, Al metal, and β' -NiAl

	Ni Metal	NiAl		Al Metal
	<u>Ni</u>	<u>Ni</u>	<u>Al</u>	<u>Al</u>
2s	1010.03(20)	—	117.72(10)	117.99(10)
2p _{1/2}	871.47(10)	870.51(10)	72.80(05)	72.84(05)
2p _{3/2}	854.22(10)	853.31(10)	—	—
3s	110.97(10)	111.12(10)	—	—
3p _{1/2}	67.87(05)	68.89(05)	—	—
3p _{3/2}	66.54(05)	67.09(05)	—	—

Table III. Comparison of FWHM of core-levels in β' -NiAl, Ni, and Al

	metal	NiAl ^b		metal
	Ni ^a	Ni	Al	Al ^c
2s	—	—	1.17(5)	1.24(5)
2p _{1/2}	1.9	1.6	.86	.95
2p _{3/2}	1.6	1.3		
3s	3.2	2.5	—	—
3p	3.6	3.2	—	—

^a Unpublished data^b This work^c Unpublished data

FIGURE CAPTIONS

- Fig. 1. Valence band density of states for β' -NiAl. Points are the experimental XPS results (this work) corrected for inelastic losses, and the dashed curve is from calculations of Connolly and Johnson (Ref. 2). The solid curve represents the theoretical curve gaussian broadened to experimental resolution (0.55 eV).
- Fig. 2. A comparison of the x-ray photoemission valence band spectra of Al and Ni.
- Fig. 3. Ni LMM Auger spectra from Ni metal and β' -NiAl. Apparent binding energies ($E_B^{(F)}$) are given relative to the Fermi energy (E_F). Kinetic energies referenced to E_F can be calculated as follows: $E_F(\text{LMM}) = 1486.6 - E_B^{(F)}$.
- Fig. 4. Ni 2p spectra from Ni metal and β' -NiAl. Binding energies are given relative to E_F .

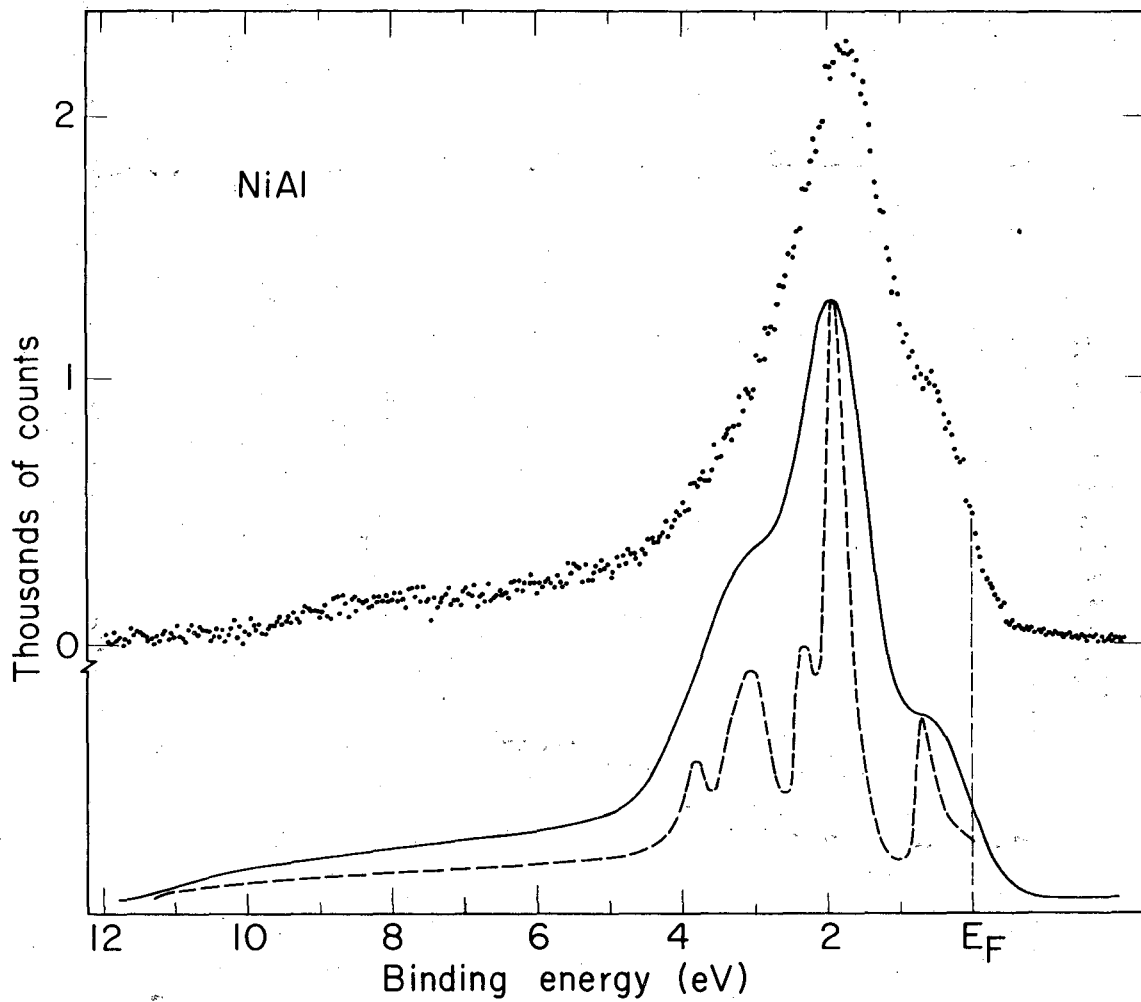


Fig. 1

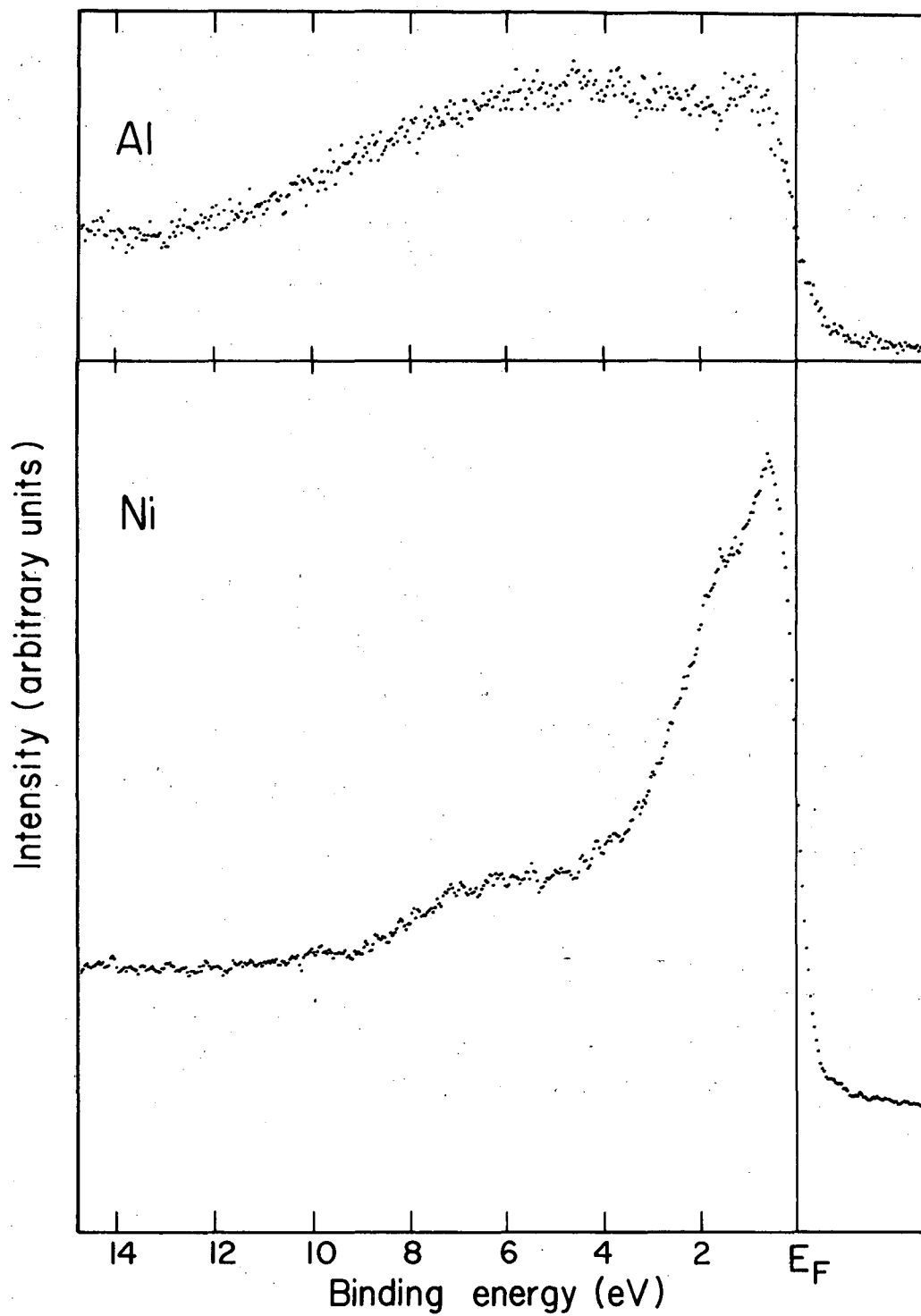


Fig. 2

XBL 773-419

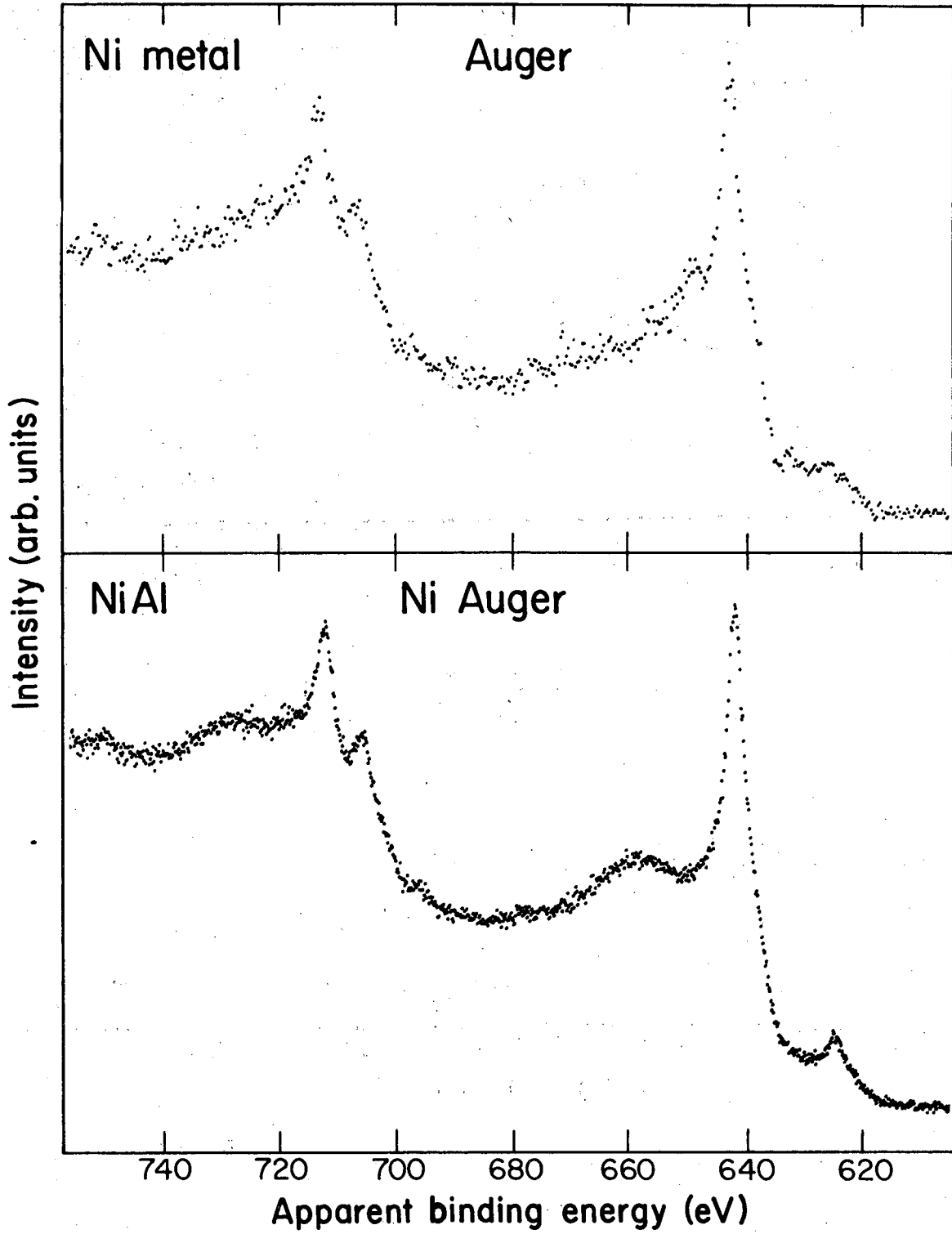


Fig. 3

XBL 772-418

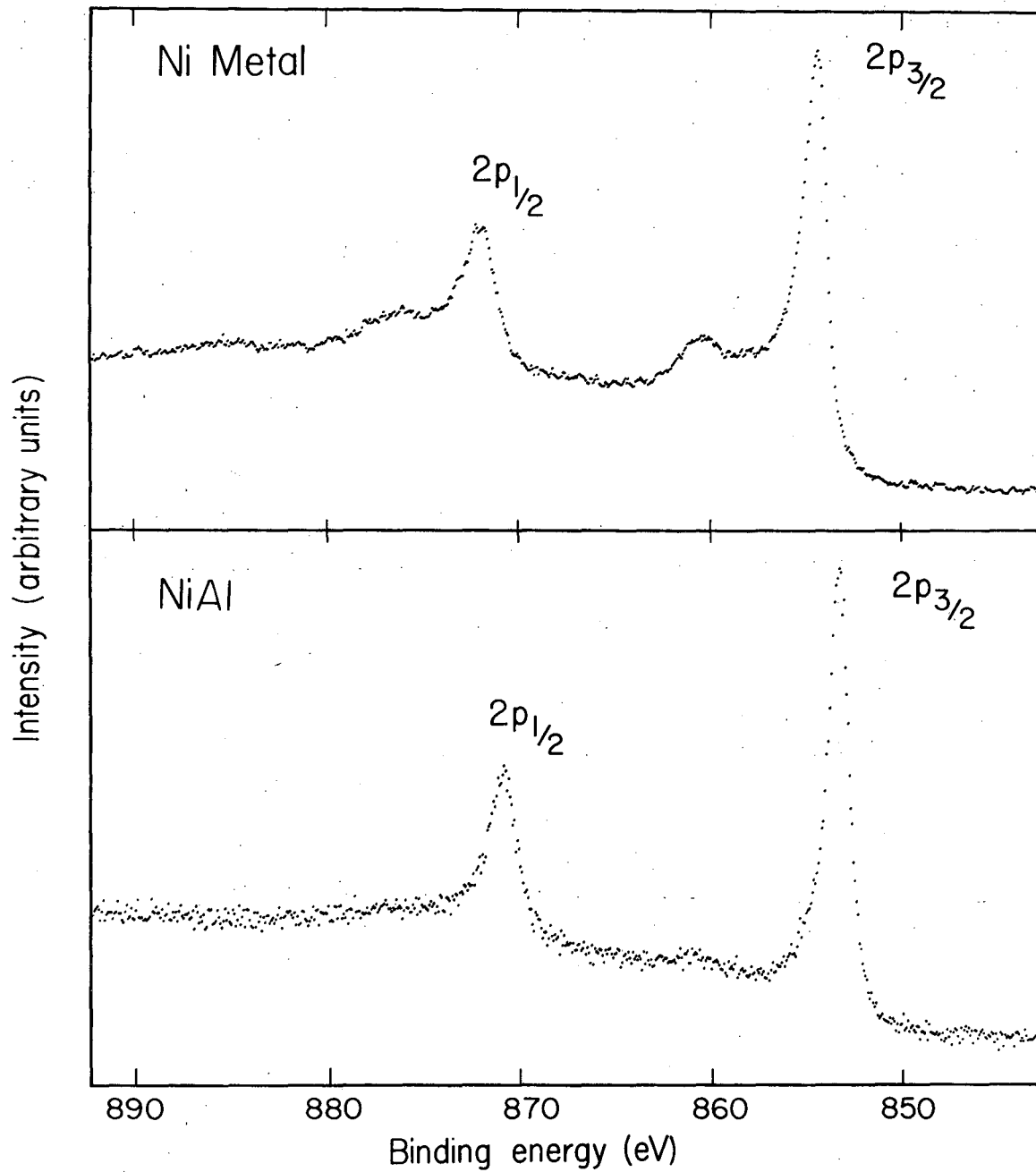


Fig. 4

XBL 772-420

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