Photoabsorption of Alloys of Al with Transition Metals
V, Fe, Ni and Cu and Pr near the Al $L_{2,3}$-Edge

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The onset of Al 2p transitions of VAl_3, $FeAl$, $NiAl$, $NiAl_3$, $CuAl_2$, $PrAl_2$ and the disordered alloys V-Al (16 at % Al, 28 %, 41 %), Fe-Al (11 %) is shifted up to 1.1 eV. New pronounced structure develops close to the onset which for NiAl agrees with a density of states calculation by Connolly and Johnson.

Der Einsatz der Al 2p Übergänge von VAl_3, $FeAl$, $NiAl$, $NiAl_3$, $CuAl_2$, $PrAl_2$ und der ungeordneten Legierungen V-Al (16 at % Al, 28 %, 41 %), Fe-Al (11 %) ist bis zu 1,1 eV verschoben. Neue starke Strukturen treten in der Nähe des Einsatzes auf, deren Lage bei NiAl mit Zustandsdichteberechnungen von Connolly und Johnson übereinstimmen.

INTRODUCTION

Soft x-ray absorption spectroscopy of alloys - in contrast to x-ray fluores-cence spectroscopy which is a well-established technique - was made possible quite recently through the application of synchrotron radiation as a con-tinuous source. The need to prepare thin alloy films of known constitution a few 100 Å thick necessitates further technical effort. After we have studied Cu-Ni (50 %) in the region of the Cu and Ni 3p transitions[1] and $AuAl_2$ in the region of the Al 2p transitions[2] it appeared to be promising to per-form a systematic investigation of Al with several transition metals and other metals.

Our investigation of Cu-Ni showed that this alloy spectrum does not deviate from a superposition of the spectra of the individual components. This demonstrates that Cu and Ni soft x-ray absorption spectra like many other spectra in this region are dominated by atomic effects. When a steep pro-minent edge occurs as in Al solid state effects must be involved and con-siderable changes on alloying are expected. There is not much structure observed near to the edge in pure Al aside from a weak "spike" right at the edge which is interpreted as a many-body-effect due to the presence of the suddenly shielded hole during the excitation process[3]. Our previous investigation of $AuAl_2$ yielded considerable structure near the onset which was at least partly explained as a density of states effect[2]. Alloys of Al with transition metals are interesting because of their high density of d-states near the Fermi level and alloys with Pr because of its f-states near the Fermi level.

Our investigation covers three distinct energy regions: (1) The region 30 - 70 eV is dominated by the 3p transitions of the transition metals and the

5p transitions of Pr, (2) the vicinity of the onset of Al 2p transitions which covers approximately the energy range 70 - 80 eV and (3) the region of Al 2p transitions into states way up in the conduction band which we have measured up to 150 eV. The latter comprises also the onset of Al 2s transitions near 120 eV. In this paper we are concerned only with the region near the Al 2p edges. A full treatment will be given elsewhere[4].

EXPERIMENTAL

The alloy films were prepared by simultaneous evaporation onto Collodion covered copper mesh from two sources (e-gun and resistance heated boat) which were kept at a constant evaporation rate. The evaporation was controlled by a quartz crystal monitor. The thickness ranged from 200 to 600 Å. The alloy films were covered with 50 Å of carbon on both sides in order to reduce oxidation and enhance mechanical stability. The efficiency of this method was tested with highly oxidizable Pr and proved to be very satisfactory. After dissolving the Collodion the films were annealed for 90 minutes at 250° C. We estimate from the accuracy of the evaporation control that the intended concentrations were obtained with an error of a few percent. The electron diffraction pattern of each alloy films was taken and it showed the correct crystal structures without any contributions from other phases.

The measurements were made using synchrotron radiation from the 7.5 GeV electron accelerator DESY monochromatized by a fixed exit slit monochromator. The measurements took special advantage from the use of a two beam densitometer described elesewhere[5]. The transmissivity of two samples could be measured simultaneously in

two channels. For the measurements reported here the alloy sample was placed into one of the light beams and a pure metal film with a thickness such that it contained exactly the same amount of the non-Al component was placed into the second light beam. Both samples were covered with the same total thickness of carbon. The ratio-spectrum[5] was recorded and can be considered to be proportional to the transmissivity of Al in its respective environment in regions where the spectrum[5] of the non-Al component is unchanged. From this transmissivity an absorption coefficient μ^f is derived. The presentation of μ^f instead of the usual absorption coefficient exhibits directly the physical quantity of interest and facilitates the discussion of the experimental results. Absolute values for μ^f and for the usual absorption coefficient of the alloys and more experimental details will be given elsewhere[4].

RESULTS AND DISCUSSION

Figures 1 and 2 give the result of our measurements near the Al $L_{2,3}$ edges. The spectra are scaled to approximately equal height of the structures. The dashed curve shows the spectrum of pure Al with its characteristic spin-orbit split $L_{2,3}$ edges. The onset of transitions at 72.6 eV is marked. The three V-Al alloys at concentrations below 50 at % Al and Fe-Al (11 %) are disordered substitutional alloys, the other alloys investigated are ordered phases. Quite generally speaking the alloy spectra show more structures than the spectrum of pure Al, the disordered alloys have broader features than the intermetallic compounds (maybe with the exception of V-Al (28 %), see below).

The onset of transitions shifts to higher (+0.4 eV) or lower energies by as much as -1.1 eV. The observed shifts within an alloy system are concentra-

tion dependend (larger shifts with lower concentration of Al). Within
the series V to Cu the shift develops also systematically from large ne-
gative shifts with V to positive shifts with Cu. A comparison of the re-
sults with shifts of the edge of x-ray fluorescence measurements by Watson
et al.[6] gives very satisfactory agreement.

In order to perform a qualitative analysis of these shifts we tried to
attribute them to individual energy changes.[4] These are shifts of the
Fermi-level due to a change in the density of states or occupation, shifts
of core levels due to charge transfer or due to a change in the effective
radius of the atomic valence shell. The measured shift will be a combi-
nation of competing effects. It was not possible to attribute the observed
shifts to a single origin.

All the alloy spectra show peaks displaced by up to 6 eV from the onset.
Especially conspicuous is the shape of the NiAl spectrum. A sharp edge is
observed quite near to its position in pure Al while another steep rise
culminating in a peak occurs at a 2.1 eV higher energy. From the electron
diffraction pattern (as mentioned above) and earlier experience with $AuAl_2$[2]
it is completely out of question that we could deal here with a two-phase
alloy. Since the peak is not located right at the edge an explanation in-
volving the "spike" effect[3] also cannot explain this feature.

Connolly and Johnson[7] have calculated the density of states of NiAl. Accor-
ding to their calculation there are two almost parallel bands above the
Fermi level which originate from s- and p-type states from Al. These bands
cause a sudden rise in the density of states at about 2 eV above the Fermi
level. The dashed curve in Fig. 3 shows the results of the density of states

calculation together with the absorption coefficient near the Al $L_{2,3}$ edge and also near the Ni $M_{2,3}$ edge. The agreement in the position of the rise with respect to the Fermi edge is very good. Also the structure at the Ni $M_{2,3}$ edge fits in although this cannot be as convincing since the Ni edge is much broader than the Al edge.

In addition the absolute change in the absorption coefficient of NiAl at the Ni $M_{2,3}$ and at the Al $L_{2,3}$ edges are compared with the values expected from a simple superposition. They are reduced to about 1/5 at the Ni edge and to about 1/3 at the Al edge.[4] The remarkable reduction of the Ni edge could be interpreted as an almost complete filling of the Ni d-states (10 electrons). A filling of these d-states is also in accordance with the phase rules which tolerate a maximum of 3 s-p electrons/unit cell for the CsCl structure (NiAl) and further it is in agreement with the measurements of the intensity ratios of x-ray fluorescence bands by Wenger et al.[8]. The reduction of the Al edge can be correlated with the specific heat measurements by Seitchick and Walmsley[9] who argue that the density of states of NiAl must be low at the Fermi energy compared to that of pure Al.

Connolly and Johnson[7] propose that the sharp rise 2.1 eV above the Fermi level in the density of states of NiAl is caused mainly by the CsCl structure of this alloy and not so much by its individual components. FeAl has the same structure and indeed the spectrum is of similar shape. If we argue along the lines of a rigid band model we could even understand the somewhat larger separation of this rise from the Fermi edge. Probably a third example of the influence of this structure is the alloy V-Al 28 %. Up to now it is not decided by crystallographic methods whether V-Al 25 % is a homogeneous solution or an intermetallic compound containing body centered V and CsCl type V-Al cells alternatively[10]. From the shape of the absorption spectrum together with the hypothesis of Connolly and Johnson we prefer the second assumption.

The structure in the other alloy spectra is not explained. Neither the
existence of empty d-bands originating from the transition metals nor the
empty f-levels of Pr appear to provide any direct explanation of the spectra.
The reason has to be seen in the vanishing overlap between the wavefunctions
of these levels with those of the Al 2p electrons. We believe that further
band calculations could help the interpretation of these spectra. Since the
spectra of the disordered phases are qualitatively not so different from those
of the adjacent intermetallic compounds, even the interpretation of these
spectra could profit from such calculations. In general it proved to be very
difficult in the past to understand core spectra of solids from band structure
calculations[11]. Apparently alloys with simple metals furnish examples where
strong density of states structures are reproduced in the soft x-ray absorption
spectra.

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Figure Captions

Fig. 1:   Absorption coefficient $\mu^{\prime}$ ("absorption of Al in the
respective alloy environment" with most of the non-Al
absorption eliminated by the two-beam technique). The
absorption of pure Al is given with the onset of the
2p-absorption marked . Absolute values of the absorption
coefficient will be given in Ref. 4.

Fig. 2:   See Fig. 1

Fig. 3:   Dashed curve: calculated density of states with the
position of the Fermi level E_F[7], solid curve: alloy
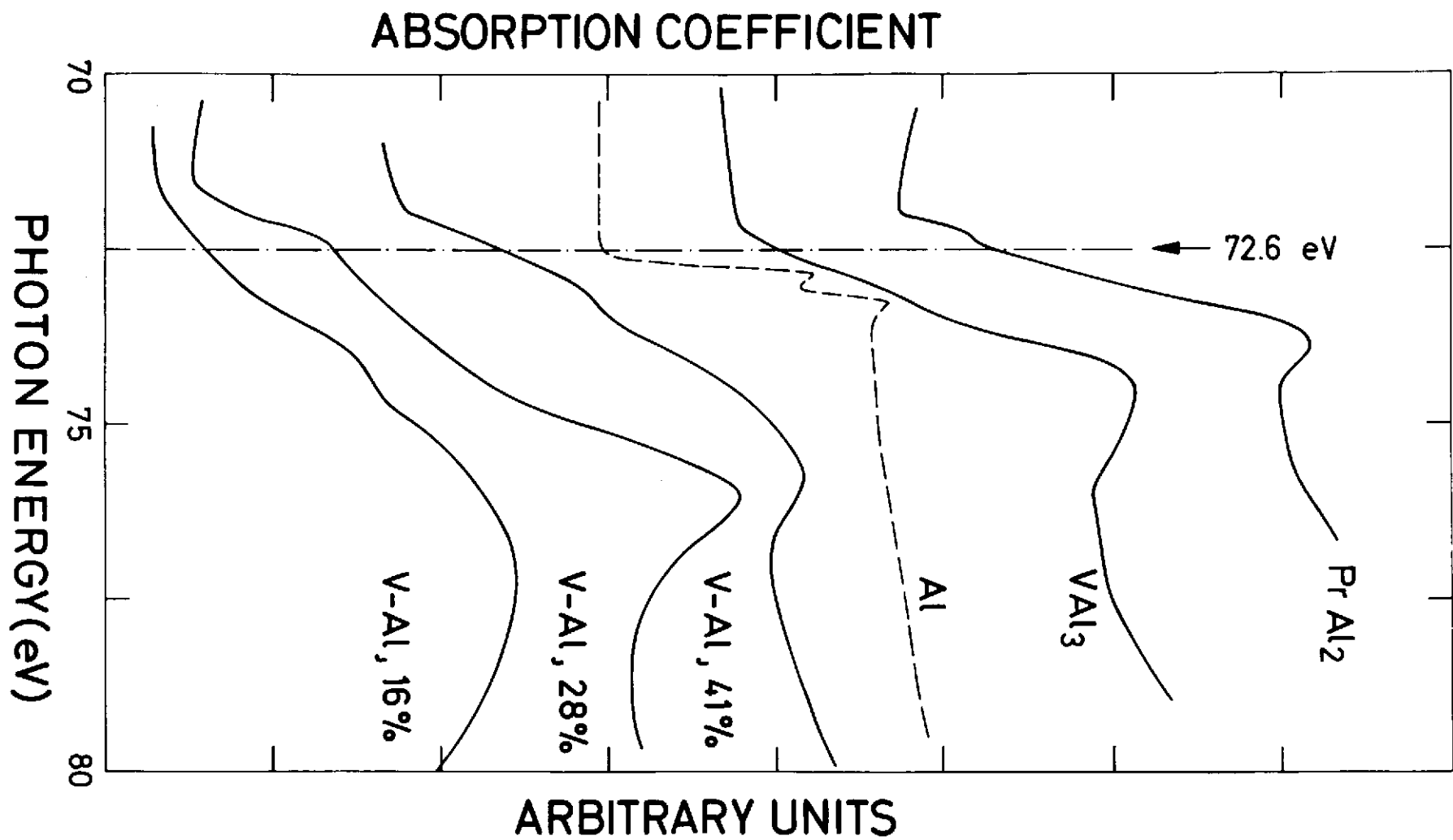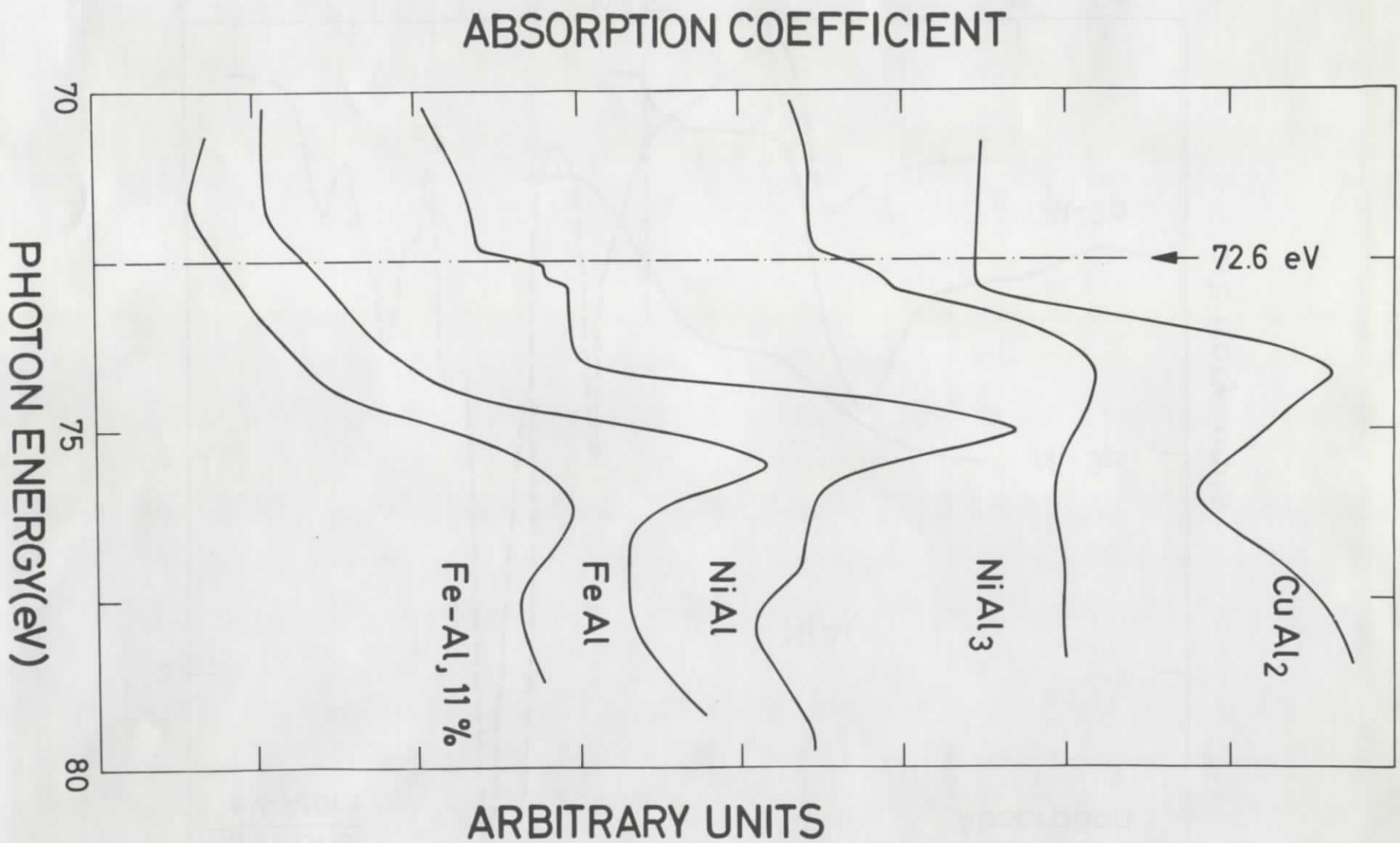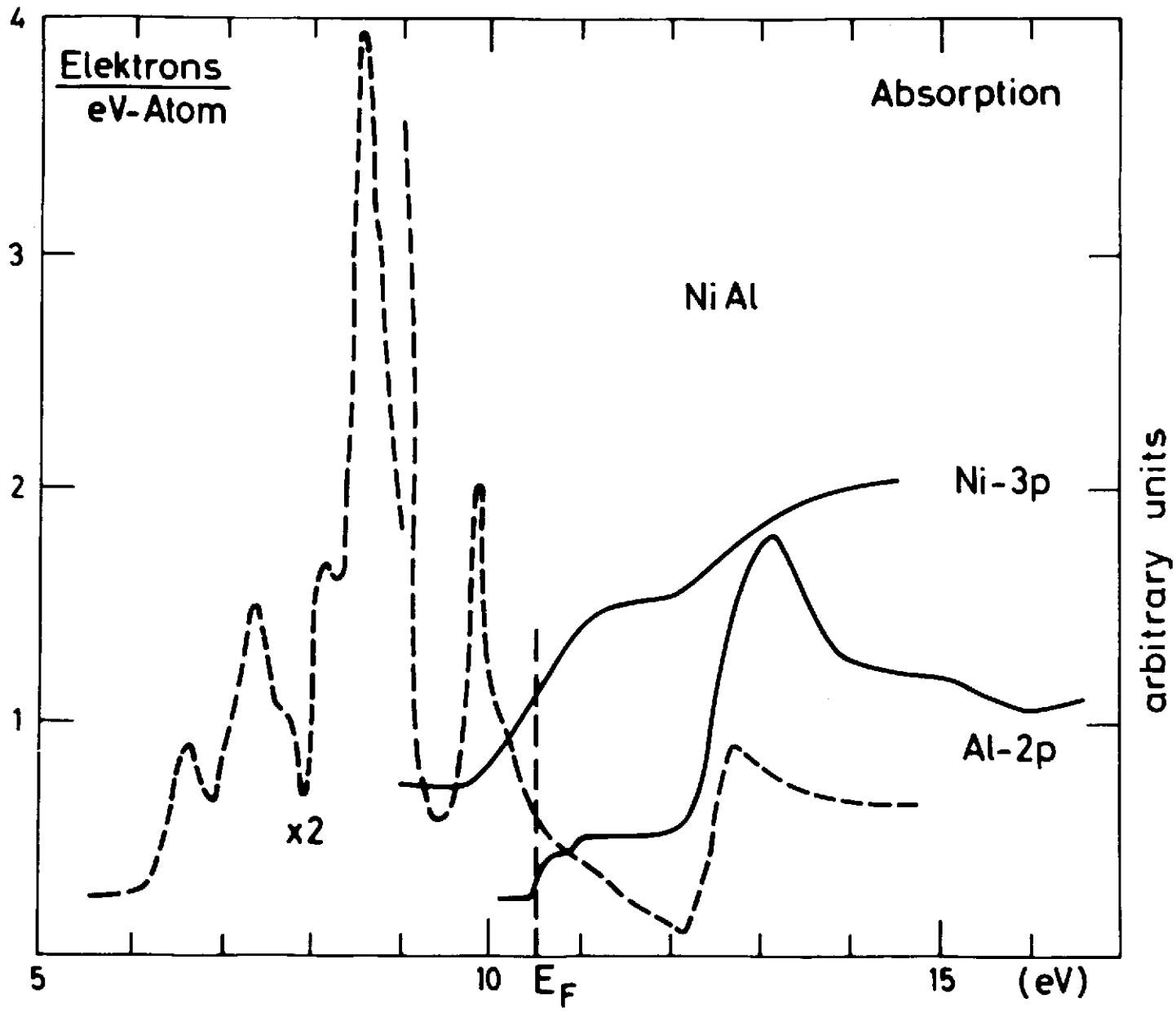spectrum, Al-2p and at Ni-3p edges fitted to E_F.

ABSORPTION COEFFICIENT

Fig. 1

Plot showing absorption coefficient (ARBITRARY UNITS) versus PHOTON ENERGY (eV) from 70 to 80, with an arrow marking 72.6 eV. Curves are labeled: V-Al, 16%; V-Al, 28%; V-Al, 41%; Al; VAl₃; PrAl₂.

Fig. 2

Fig. 3