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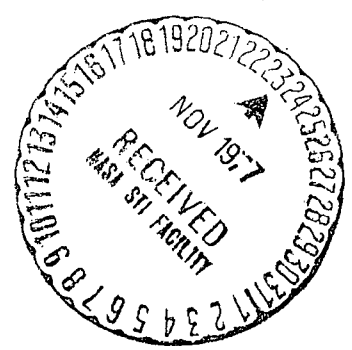
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EVOLUTION OF ION EMISSION YIELD OF ALLOYS WITH THE NATURE
OF THE SOLUTE. II. INTERPRETATION

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16. Abstract

Solid solutions of transition elements in copper, nickel, cobalt, iron, and aluminum matrices were analyzed by observing secondary ion emission under bombardment with 6.2-keV argon ions. Enhancement of the production of solute-element ions was observed. An ion emission model is proposed according to which the ion yield is governed by the probability of an atom leaving the metal in a preionized state. The energy distribution of the valence electrons of the solute atoms is the bases of the probability calculation.

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EVOLUTION OF ION EMISSION YIELD OF ALLOYS WITH THE NATURE
OF THE SOLUTE. II. INTERPRETATION

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national de la recherche scientifique, National Council
of Scientific Research]

1. Presentation of a model.

The atomic particles ejected during bombardment of a target
have energy with a spread between a fraction of one electron-volt
and several hundreds of electron-volts. Their velocities are so weak
that one cannot assume that the conduction electrons at the Fermi
level, which are much more rapid, remain in a neutral state at the
moment of their exit from the metal. From this observation it
follows that the process of ionization cannot occur except outside
the metal and in the condition that the atom carries, in its elec-
tron procession, an energy of excitation higher than the ioniza-
tion energy. Then one has a case of auto-ionizing states [1].

In order to determine the probability of the formation of
auto-ionizing states, one has to follow the evolution of the
electron structure of the atom during its motion in the metal from
its crossing of the surface up until it has sufficient elongation
not to interact with this surface any longer.

The difficulties of such a rigorous approach have led us to
construct a simple model, going from known experimental data.
Also, photon emission of the ejected atoms belonging to the first
transition series shows the existence of numerous strongly excited
states in which an electron of the d shell participates [2-3].
This suggests that the auto-ionizing states of even higher energy
are themselves the result of excitation of at least an electron

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*Numbers in the margin indicate pagination in the foreign text.

of the d shell. To put it another way, the auto-ionizing states responsible for ion emission are, at departure, carriers of a hole on the d shell. We have shown that the existence of this hole was a necessry but not sufficient condition for the state to be auto-ionizing because it must be no more than the energy divided among the electrons outside the d shell, being too high for a spontaneous deexcitation of the atom following its ionization [4].

A very diagrammatic description of the exit of the atom, which uses a frequently assumed hypothesis for problems of the surface [5] makes it possible to reach a simple formulation of the probability of the formation of auto-ionizing states. This hypothesis consists of introducing a critical distance x_c beyond which the particle can be considered as free, and to assume that the balance of the electron structure of an atom can be translated, in x_c, as a transition of electrons occupying the states near to the Fermi level toward the states of a free atom [4]. Beyond x_c, electron changes remain possible still, and can lead to a modification of the proportion of auto-ionizing states obtained in x_c, destroying a small part of them [6].

If one defines a probability $F_d(v)$ for an atom expelled with velocity v, one finds in x_c with a d hole and a probability $P_{x_c}(E_m-\delta-E_F)$ for the energy of electrons outside the d shell as being higher than the energy of ionization, the probability for an atom being in an auto-ionizing state will be equal to the product of $F_d(v)P_{x_c}(E_m-\delta-E_F)$. In our model, the calculation of $P_{x_c}(E_m-\delta-E_F)$ rests on the hypothesis that the electrons which remain excited, during transition to x_c, retain the same baryonic center of energy [4]. It is a question then of determining the probability at which these electrons taken in the metal will have a baryonic center of energy located above a certain value E_m corresponding to the first auto-ionizing state. If E_F is the

departure work and δ is the energy of excitation of the ion formed, electrons in which the baryonic center is located between the Fermi level and the $E_m - \delta - E_F$ level are the only ones which occur in the formation of auto-ionizing states (Fig. 10 in the Appendix). It is natural that the level drops in the section of states occupying the conduction band, that is to say, that $E_m - \delta - E_F$ is positive.

The probability $P_1(v)$ that an atom expelled with velocity v shows that a secondary ion is the result of possible breakdown of auto-ionizing states by interaction of the atomic surface beyond x_c. One can point out [6] that probability $P_0(v)$ that an auto-ionizing state escapes this destruction by increases with v and approaches unity for particles emitted with a kinetic energy above 30 eV.

Finally, one then has:

$$P_1(v) = F_d(v) \, P_{x_c}(E_m - \delta - E_F) \, P_0(v).$$

(1)

This probability of ionization corresponds with the rate of ionization of atoms expelled with velocity v, which was defined in the first section. In the case of an $A_{1-c}B_c$ alloy, one has for each of the elements:

$$P_1(B^+) = \frac{K_c(B^+)}{c S_{AB}} \text{ and } P_1(A^+) = \frac{K_{1-c}(A^+)}{(1 - c) S_{AB}}.$$

(2)

As we have already indicated, one can easily obtain the relationships of ionic yields from ions emitted at a given energy by testing. If one has carried out measures on ions of energy which are too high, so that $P_0(v)$ will be practically equal to one, one has

$$\frac{K_c(B^+)}{K_{1-c}(A^+)} = \frac{c P_1(B^+)}{(1-c) P_1(A^+)} \#$$

$$\frac{P_{AB}^B(E_m - \delta - E_F)}{P_{AB}^A(E_m - \delta - E_F)} \cdot \frac{F_{AB}^B(v)}{F_{AB}^A(v)} \cdot \frac{c}{1 - c}.$$

(3)

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In this expression, P_{AB}^A and P_{AB}^B on one side, F_{AB}^A on the other, represent the probabilities P_{xc} and F_d relative to the AB alloy and its elements A and B. Experience shows that the energy distributions of the A^+ and B^+ ions, coming from alloys between transition metals, are homothetic if the energy of emission is above 30 eV [7]. The relationship $F_{AB}^B(v)/F_{AB}^A(v)$ is then independent of the speed of ejection of ions which are sufficiently fast. This observation inspires us, at the first stage, to compare the experimental values of ion constants

$$\frac{1-c}{c} \frac{K_c(B^+)}{K_{1-c}(A^+)} = k_{AB}^E \quad (E > 30\,eV)$$

and the calculated relationship $P_{AB}^B/P_{AB}^A = \chi_{AB}$. For a series of alloys of the same matrix, one returns in some way to take in a probability of the formation of a constant d hole for the dissolved elements and for the matrix. We will examine this point a little later on, discussing a possible modulation of emission for probability F_d.

In aluminum alloys with an element of transition T at which one no longer has similarity between energy distributions of the T^+ and AL^+ ions, one will simply compare the yields of $K(T^+)$ to the probabilities $P_{AlT}^T(E_m-\delta-E_F)$.

The explicit calculation of $P_{x_c}(E_m-\delta-E_F)$ necessitates knowledge, on the one hand, of the nature of auto-ionizing states and their density $g(E)$ on the atom and, on the other hand, of density $n(\varepsilon)$ of the initial electron states in the metal.

Examination of energy distributions of the ions emitted, assuming the condition $E_m-\delta-E_F>0$, we have retained two types of auto-ionizing structures in the alloys being studied [6]:

-- for copper:

$$3d^{v-1}\,nl\,n'l' \rightarrow (3d^v)^+ + e$$
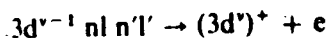
-- for elements of titanium in nickel:

$$3d^{v-2}\,nl\,n'l'\,n''l'' \rightarrow (3d^{v-1}\,4s)^+ + e.$$
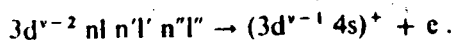
One sees, from these two structures, that it leads to consideration of excitation of two electrons in the first case, and three electrons in the second. The values of $E_m-\delta-E_F$ which follow from these structures are recalled in Table 1.

TABLE 1
VALUES OF $E_m-\delta-E_F$

Matrices	Elements in solution							
	Ti	V	Cr	Mn	Fe	Co	Ni	Cu
Fe	+ 1.18	+ 1.35	+ 1.25	+ 1.1		+ 0.85	+ 1	+ 1.1
Co	+ 1	+ 1.19	+ 1.09	+ 0.93	+ 0.75		+ 0.85	+ 0.95
Ni	+ 0.6	+ 0.79	+ 0.7	+ 0.55	+ 0.35	+ 0.3		+ 0.55
Cu	+ 1.03	+ 1.2	+ 1.1	+ 0.95	+ 0.75	+ 0.7	+ 0.85	
Al	+ 1.22	+ 1.4	+ 1.3	+ 1.14	+ 0.95	+ 0.9	+ 1.05	+ 1.15

We will assume in the series of calculations that density g(E) of auto-ionizing states of the atom is constant.

Because of the density of the states $n(\varepsilon)$, one knows that in most of the alloys, the solute atoms have their own electron structure localized in a volume on the order of atomic volume, and that it is very different from the electron structure of atoms of the matrix. One can ask then if the auto-ionizing states of solute atoms are caused by electrons which travel from the conduction band of the matrix or if, on the other hand, they

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are the result of electrons well-localized around the atom. The first eventuality causes one to take the same electron density $n(\varepsilon)$ to explain ion emission of diverse types of atoms and one sees then that it directly attests to the fact that it can play the role of a matrix in the over-excitement phenomena which we have observed. The second eventuality leads one to take electron densities which are different for the two types of atoms and then again the matrix controls the mechanism of emission of solutes where the electron structure of the latter depends on the metal in which it is dissolved.

We have first tested the first eventuality which was found very often not to conform to experimental results [8-9]. One should always emphasize that the electrons of the matrix can intervene with the emission process of slow ions where they are responsible for breakdown of part of the auto-ionizing states [6].

In this article we will examine the second eventuality, that is, that the local electron structure of the atom can interfere in the ionizing mechanism.

One shows in addition that the probabilities $P(E_m-\delta-E_F)$ are equal to:

$$P(E_m-\delta-E_F)=\frac{R(E_m-\delta-E_F)}{\frac{1}{2}N_0^2} \text{ or } \frac{R(E_m-\delta-E_F)}{\frac{1}{3}N_0^3}$$

as 2 or 3 electrons intervene in the auto-ionizing structure. N_0 is the number of electrons d + s of the atom and the function $R(E_m-\delta-E_F)$ is the result of a convolution on electronic density $n(\varepsilon)$ of the atom in the metal on the field of energy which occurs between $E_m-\delta$ and E_F.

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2. A comparison of experimental ion constants k_{AB} of alloys and the relationships calculated of probabilities of formation of auto-ionizing states χ_{AB}.

In substituting an element of transition of an atom of pure metal in order to form an alloy, one introduces an excess or a deficiency of electrons equal to the difference of the Z valence of atoms of metal and the element of transition. Electrostatic equilibrium of the metal alloy requires that the dissolved atom maintain its electrical neutrality in an atomic volume of about (10). This filtering is the result of distribution of a group of electrons with the valence of the dissolved atom on the states in which density is, in general, different from the density of the states of the matrix. It is the distribution in energy $n(\epsilon)$ of these electrons that we have described in order to deduce finally the probabilities of ionization. This description applies, more precisely, to the d electrons which are found distributed in the densest states localized in a narrow field of energy. The important number of these electrons and their distribution are the factors which determine the efficiency of the ionization process analyzed from the local electron structure. On the other hand, the electrons of conductibility, less numerous and distributed on low-density states, more extended in energy would contribute little to the ionization process.

The alloys are classed in two categories:
-- those in which the electron structure does not have a resonant state,
-- and those which carry a resonant state or a potential bound state [10].

The numerical calculations of probabilities of the formation of auto-ionizing states have been made from simple analytical expressions approaching, at best, electron densities; some of the results already pointed out in reference [4] are repeated simply in the Appendix.

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2.1. Alloys which do not have a resonant state.

2.1.1. Alloys on a base of nickel and cobalt which contain impurities from the neighboring valence: NiCo; NiFe; NiMn; CoNi; CoFe; CoMn.

The d bands of ferromagnetic nickel and cobalt are separated into two halves containing opposite spin electrons d_+ and d_-. The Fermi level uniquely intercepts the highest energy d_- half-band [11]. When one alloys these two metals and elements of the neighboring valence, the excess or deficiency of electrons carried by the solute modifies filling of the d_- half-band of highest density at the Fermi level without changing the shape itself of the density of the states too much (this corresponds to a model with rigid bands [10-12]).

To the extent that deformation of the density of the states close to the Fermi level is weak, one can estimate the probability of the formation of auto-ionizing states P_{AB}^B in using the parameters of density of the states of pure matrices of nickel and cobalt.[1]

If N is the number of electrons d + s of an atom of the ma- /246trix and N + Z that of a solute atom, one finds

$$\chi_{AB} = \frac{(E_m - \delta - E_F)^3_{solute}}{(E_m - \delta - E_F)^3_{matrix}} \cdot \left(\frac{N}{N+Z}\right)^3$$

in using the approximate expressions of density of constant states (§4 in the Appendix).

---

[1] The appearance of an antiresonant state at the height of the d_+ band has little effect on the probability of ionization given the fact that electrons located at this level are too far below the Fermi lever to participate effectively in the formation of auto-ionizing states.

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The values are the following:

Matrices		Mn	Fe	Co	Ni
Ni	Z	-3	-2	-1	0
	χ_{AB}	5	0.9	0.41	
Co	Z	-2	-1	0	+1
	χ_{AB}	4.5	1.7		1.3

In reporting the experimental results presented in the first section, one can state that χ_{AB} is in good agreement with the ion constants measured (Figs. 1 and 2).
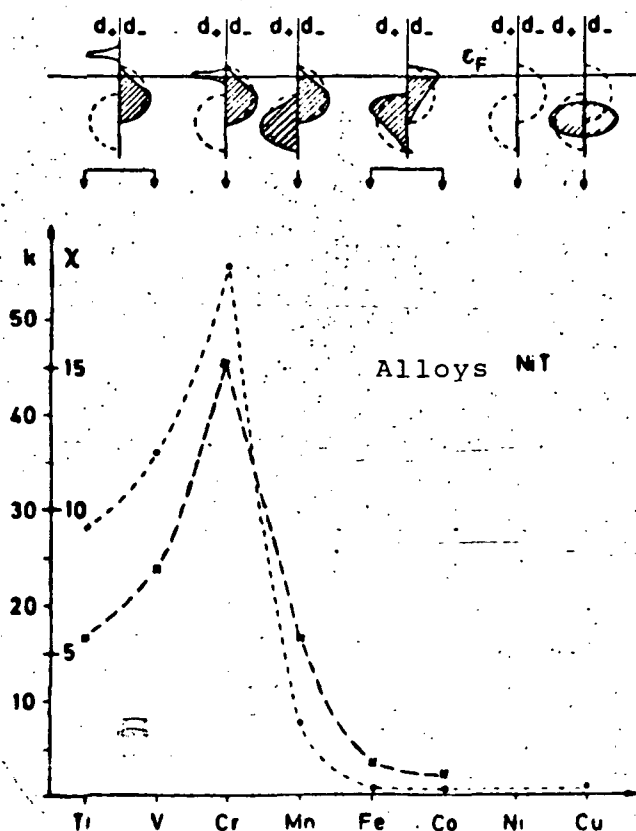

Fig. 1. Emission of elements of transition T in solution in nickel; ● measurements of ion constants k; X calculations of χ.

2.1.2. Alloys of nickel and cobalt containing non-magnetic impurities: NiCu; CoCu.

In the first series of transition elements, stability of d orbitals increases with the atomic number [14]. This involves, for an element at the end of a series such as copper in solution in cobalt or nickel, a lowering of the energy of the d states below the Fermi level of the matrix. One observes well, experimentally, that the density of the d states on copper is practically zero at the Fermi energy [15]. The electron structure of copper is made up here of a zone with strong density
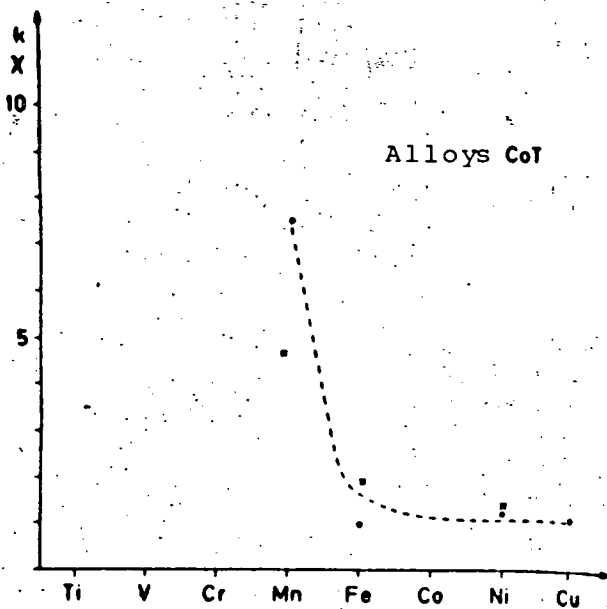
Fig. 2. Ion emission of elements of transition T in solution in cobalt: ● measurements of ion constant k; X calculations of χ.

states containing the complete shell of d electrons topping a band of weak density conductibility. In its form, this structure quite resembles that which one finds in pure copper (Fig. 11a Appendix) except for differences in the width and position of the d band. One does not have any precise data for these two parameters in order to calculate the probability of formation of auto-ionizing states of copper in these alloys. However, one could remark that this structure must have probabilities which are too weak comparable to those of pure copper due to lowering of energy of the d states, high density, slightly below the Fermi level.

In simply transposing electron density of pure copper to each of the alloys, one would obtain the probabilities on the same order $P_{\underline{Ni}Cu}^{Cu} \sim P_{\underline{Co}Cu}^{Cu} \sim P_{Cu}^{Cu}$, which explains qualitatively that the coefficients of excitation measured are in the neighborhood of one:

$$P_{\underline{Ni}Cu} \sim P_{\underline{Co}Cu} \sim 1.$$

2.1.3. Alloys on an iron base: FeCo, FeMn, FeCr, FeV.

The complexity of the structure of the band of iron makes study of these alloys very difficult. In the model developed by Gomes [16], the density of the states for each of the spin directions of the d band is represented by two identical parabolas
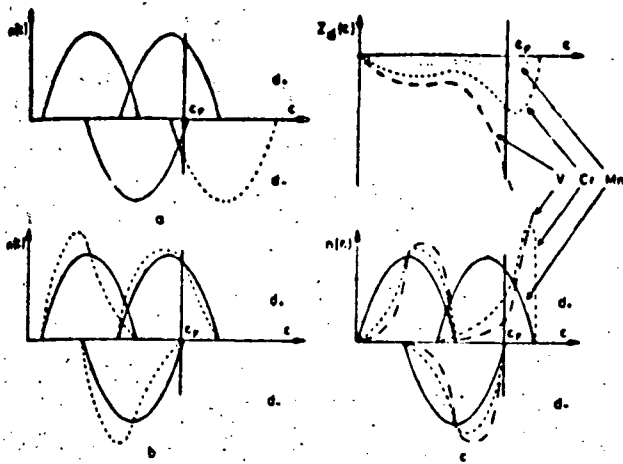
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Fig. 3. Electron structures of alloys on an iron base according to Gomes [16]: a) structure of the iron band; b) electron density of cobalt in iron; c) shifting of $Z_d(\varepsilon)$ charges and electron densities of V, Cr, Mn.

which overlap in part (Fig. 3a). The energy divergence of the two half-bands is such that the Fermi level drops in the zone of strong d_+ density and weak d_- density. Then there will be a majority of + spin electrons located close to the Fermi level which will contribute most to shielding from the impurity. This shield results from a dis- placement of the $Z_d(\varepsilon)$ charges and consequently from a change in density of the d states of the iron

$$\Delta n(\varepsilon) = \frac{dZ_d(\varepsilon)}{d\varepsilon}$$

around the impurity. When one dissolves manganese, chromium or vanadium, the balance of this operation results in elimination of one, two or three charges in such a way as to maintain the neutrality of the atomic cell. On the other hand, when cobalt is dissolved, an additional charge is added.

The calculations developed by Gomes give the expressions $\Delta n(\varepsilon)$ and consequently, the probability formation of auto-ionizing states is in principle calculable by taking a density of the states $n_d(\varepsilon) + \Delta n(\varepsilon)$ around each impurity. However, the complicated forms of the d band of iron and the $\Delta n(\varepsilon)$ expressions make this calculation difficult. On the other hand, the approximations which we make are too rough to be able to correctly deduce the method of precise numerical calculation. For these reasons, we have preferred to discuss qualitatively, according to the Gomes model, the
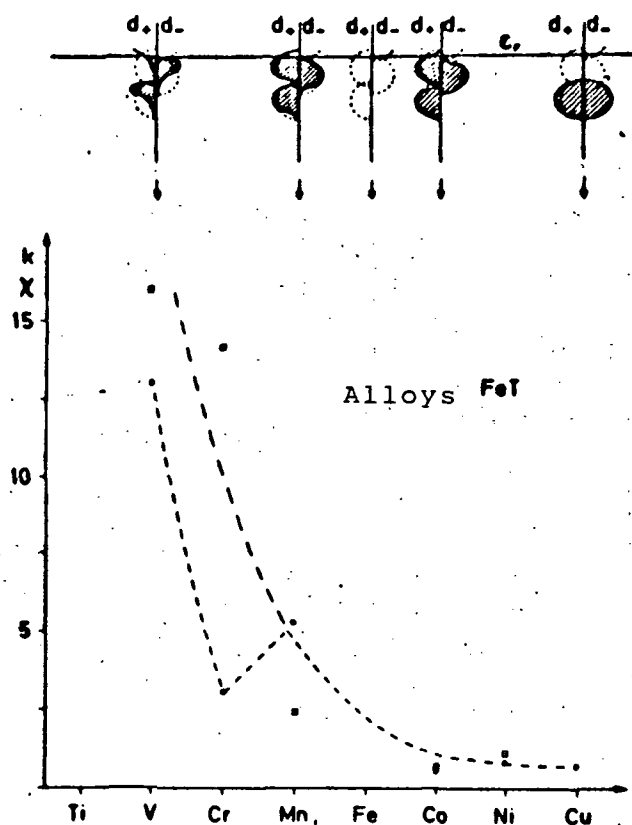
Fig. 4. Ion emission of the elements of T transition in solution in iron: ● measurements of ion constants k; X calculations of χ.

form of densities of the states around the impurities (Fig. 3) and to directly deduce the concept of evolution of the probabilities of ionization.

If the potential disturbance created by the impurity is weak, the $Z_d(\varepsilon)$ charge displaced by the ε energy is proportional to the density of the $n_d(\varepsilon)$ states of iron [16]. This is approximately the case for manganese, for which deformation of the d band is slight. Likewise, for cobalt, deformation close to the Fermi level is very weak. One can then have an estimation of probabilities P^{Mn}_{FeMn} and P^{Co}_{FeCo} in using the d band of iron. One then finds $\chi_{FeMn} \sim 2$ and $\chi_{FeCo} \sim 0.75$, values which show well the increase in ion emission of cobalt to manganese (Fig. 4).

The d band of iron contains 7.2 electrons/atom, that is to say, 2.5 in each of the two full parabolas and 2.2 in the third, which is intercepted by the Fermi level. But for impurities with valence lower than that of iron, such as chromium and vanadium, the largest part of elimination of charges results in this latter parabola. One could then consider that it is practically vacant around chromium and vanadium after 2 and 3 charges have been repelled. The electron structure of these impurities can be placed side by side with the two deformed parabolas in the same manner and contain very

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close to the same number of electrons. The approximation of a
constant for a width $\Delta \sim 4.5$ eV, does not seem very unreasonable in
a case where one is carrying out an approximate calculation. The
probabilities are then, respectively

$$P_{\underline{Fe}Cr}^{Cr} \sim 8.5 \times 10^{-2} \quad \text{et} \quad P_{\underline{Fe}V}^{V} \sim 10^{-1}$$

in which

$$\chi_{\underline{Fe}Cr} \sim 14 \quad \text{et} \quad \chi_{\underline{Fe}V} \sim 16.$$

The result for vanadium is in good accord with the experimental
ion constant ($k_{exp} \sim 13$) but it is much higher than that of chromium
($k_{exp} \sim 3$) (Fig. 4). In reality, one must not attach too much im-
portance to numerical values, given the very approximate diagram
used for describing the electron's structure. Qualitatively, on
the other hand, the increase of the ion constant which one finds
when the valence of the impurity decreases, is interpreted well   /248
by the fact that the electrons are more and more repelled across
the Fermi level, which then increases the probability of the for-
mation of auto-ionizing states.

2.1.4. Alloys on a base of iron containing nickel and nonmagnetic
elements: FeNi and FeCu.

The two additional electrons of nickel or the three of cop-
per have not been found to lodge in the d half-band almost full of
iron where there are only 0.3 holes available per atom. Shielding
is then assured by filling of the empty parabola of the d_ states.
One then has a total of 2.5 + 0.3 places. In these conditions, it
is probable that the d electrons localized around the copper atom
together fill the d states in the same way as in an NiCu alloy.
One would not expect then to find an emission of Cu^+ ions almost
identical in the two FeCu and NiCu alloys, and this is what exper-
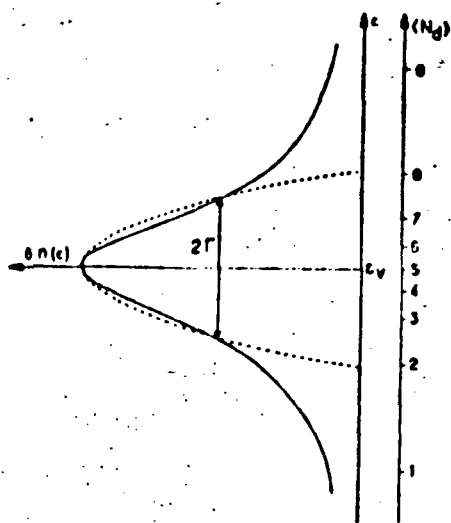ience shows when $p_{\underline{Ni}Cu} \sim p_{\underline{Fe}Cu} \sim 1$.

Figure 5

The electron structure of nickel in solution in iron is not sufficiently well known to be able to calculate the probability of the formation of auto-ionizing states. Preserving the structure of the band of the iron matrix, one obtains $X_{FeNi} \sim 1.8$, a value which is close to the ion constant (Fig. 4). Although obtained in a very arbitrary manner, this result cannot be, however, extended to that which gives a more exact model of the electron's structure.

2.2. Alloys having a resonant state or a potential bound state.

It frequently occurs that the atomic d level of an element of transition in solution is found immersed in the band of conductibility of the matrix too close to the Fermi energy. The level is enlarged in order to form a potential bound state by resonance with the d components of the dissolved state of the conduction band [17]. The energy states involved with this resonance are divided into a small band with width 2Γ centered around an energy ε_v (counted from the bottom of the conduction band) (Fig. 5). There is then locally an excess of density of states which can contain the charge of the initial state, that is to say, 10 electrons at a maximum for a d level.

This phenomenon occurs in AlT, CuT and also in the alloys between transition metals where the valence of a solute is very much weaker than that of the matrix, as for example NiCr.

The addition of density of the states per unit of volume $\delta n_d(\varepsilon)$ of the potential bound state varies like a Lorentzian centered on the energy ε_v [17] (Fig. 5)

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$$\delta n_d(\varepsilon) = \frac{2(2l+1)}{\pi} \frac{\Gamma}{\Gamma^2 + (\varepsilon - \varepsilon_v)^2}. \qquad (4)$$

This approximate expression fixes the width 2Γ very well for the potential bound state so that one can deduce the measurements of specific electron heat and resistivity. The mean number $<N_d>$ of d electrons contained in the potential bound state is equal to

$$\langle N_d \rangle = \int_{-\infty}^{\varepsilon_F} \delta n_d(\varepsilon)\, d\varepsilon = \frac{2(2l+1)}{\pi} \text{arc cotg} \frac{\varepsilon_v - \varepsilon_F}{\Gamma} \qquad (5)$$

where ε_F is the Fermi energy counted from the bottom of the conduction band of the matrix.

Calculation of the probability of formation of auto-ionizing states is carried out in the following manner:

-- One chooses a reasonable value of the width 2Γ of the potential state. This is maintained constant in a determined matrix. Then one ignores widening involving setting up a resonant state [17].

-- Knowing the number $<N_d>$ of d electrons, one deduces the position of the center of the resonant state by relationship to the Fermi energy.

-- Finally, one calculates the probability $P(E_m-\delta-E_F)$ using the values $E_m-\delta-E_F$ of Table 1. One can write this probability in the form

$$P(E_m - \delta - E_F) = \frac{R_{d^3} + R_{d^2s} + R_{ds^2} + R_{s^3}}{\frac{1}{3} N_0^3} \qquad (6)$$

in the case where auto-ionizing states carry three excited electrons. N_0 is the total number of d and s electrons of the atom in solution;

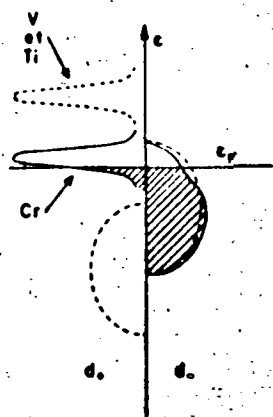$$R_{d^3} + R_{d^2s} + R_{ds^2} + R_{s^3}$$

Fig. 6. Electron structures of Ti, V, Cr in nickel.

represents the number of triplets of energy states favorable to the formation of auto-ionizing states; R_{d^3} relates to three states taken in the d band, R_{d^2s} two states of the d band and a band of conductivity s (the electrons of conductivity will always be designated by s) and so forth. In many alloys, the most important term comes from R_{d^3} and we can limit ourselves to estimating it.

The method of positioning ε_v becomes in- applicable when the potential state is completely full, or at least very imprecise when it is close to filled or almost empty. The density of the Lorentzian state shows, in effect, too important an enlargement in energy (Fig. 5) which causes, for extreme situations, the center ε_v of the resonance to be found rejected very far below the Fermi level or, on the contrary, too high, which corresponds more to the idea of a potential state very localized in energy. In this case, one could use direct experimental measurements of the center of resonance, for example, by photoemission [18-20].

For convenience in calculation, one could equally well have used a parabolic density of the states (Fig. 5)

$$\delta n(\varepsilon) = \frac{2(2\,l + 1)}{\pi \Gamma}\left[1 - \frac{(\varepsilon - \varepsilon_v)^2}{b^2\,\Gamma^2}\right] \tag{7}$$

adjusted as well as possible to density of the Lorentzian states by means of the parameter b (calculations in the Appendix).

2.2.1. Alloys on a base of nickel and cobalt containing impurities of very distant valence: NiCr, NiV, NiTi.

When the potential of the impurity is strongly repellent, the d_+ states are repelled at the Fermi level and then form a potential bound state. In the first series of transition, this effect appears when the difference of Z valence of the solute and of the matrix is higher than or equal to 4 for alloys on a nickel base [13, 15, 21]. Then, starting with chromium, there is a formation of a resonant state at the Fermi level.

The electron structures of chromium, vanadium and titanium are shown diagrammatically in Figure 6. They are made up of a resonant d_+ state of narrow width, $2\Gamma \sim 0.3$ eV and a d_- of nickel more or less deformed according to the nature of the impurity [13, 22-24].

For chromium, the d_+ state contains an electron of about $(N_+=1)$ and a d_- half-band of 4.5 electrons ($N_-=4.5$). The deformation of this band is very slight here Fig. 6). The probability $P_{\underline{Ni}Cr}^{Cr}$ is equal to

$$P_{NiCr}^{Cr} = \frac{R_{d\lambda} + R_{d^2,d_-} + R_{d,d^2} + R_{d^3}}{\frac{1}{3} N^3}.$$

To calculate this expression, one assumes that the electrons of the potential d_+ state are localized at Fermi energy (this is proven by the fact that $2\Gamma \sim 0.3$ eV is small) and that the density α_- in the d half-band is constant. As $E_m - \delta - E_F = 0.7$ eV is larger than the width 2Γ, all the electrons of the d_+ state participate in the formation of auto-ionizing states.

Then one has

$$R_{d\lambda} = \frac{1}{3} N_+^3$$
$$R_{d^2,d_-} = \frac{1}{2} N_+^2 \, 3\alpha_-(E_m - \delta - E_F)$$
$$R_{d,d^2} = N_+[\frac{3}{2}\alpha_-(E_m - \delta - E_F)]^2$$
$$R_{d^3} = \frac{3}{2}\alpha_-^3(E_m - \delta - E_F)^3$$

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N=6 for chromium and it has retained the value α ~1.1 electron/atom.eV in uniformly distributing the 4.5 electrons of the d_ band on a width Δ~4 eV, being 1 eV less than the total width of the d band of nickel. This difference of 1 eV corresponds to the divergence of the d_+ and d_ bands [11].

One finds $P_{\underline{Ni}Cr}^{Cr}$ ~4×10⁻², or $\chi_{\underline{Ni}Cr}$ ~15. With an electron less than that of vanadium, the potential bound level is open. For titanium, an additional electron is then removed from the d_ band. In these two cases, the d_ density is repelled across the Fermi energy. Not having any way of knowing this density, we assume it always to be constant, but it is certain then that the results will be deficient. One finds

$$P_{\underline{Ni}V}^{V} \sim 2.5 \times 10^{-2} \text{ and } P_{\underline{Ni}Ti}^{Ti} \sim 2 \times 10^{-2}.$$

in which

$$\chi_{\underline{Ni}V} \sim 8 \text{ and } \chi_{\underline{Ni}Ti} \sim 7.$$

If one refers to Figure 1, one sees that in the series of alloys on a nickel base, the calculated values of χ_{AB} show the same evolution as experimental ion constants. In particular, one can state that the peak observed at the level of chromium seems to be well-related to the appearance of a potential bound state in which the electron density at the Fermi level is very high.

2.2.2. Alloys CuT.

The width of the potential bound state is estimated at 1 eV. It should be noted always that this choice is not impera-tive. It simply represents a reasonable order of magnitude jus-tified by theoretical considerations [17] and by experimental measurement [18-20].

One fixes the position of the center of a potential bound state by relationship to Fermi energy as a function of its filling. For certain alloys, one must also take into account the decoupling following the two directions of spin. This decoupling exists for vanadium, chromium, manganese and iron, but does not exist for titanium, cobalt and nickel. The degree of occupation of the two states of spin is indicated in Table II [25]. One notices that d_-

is completely empty for vanadium and chromium, while for manganese and iron d_- is partially filled and d_+ is full.

TABLE II

TABLEAU II

	Ti	V	Cr	Mn	Fe	Co	Ni
N_{d_+}	1.5	2 ou 3	4	5	5	4.25	4.5
N_{d_-}	1.5	0	0	0.7	1.2	4.25	4.5
$N_{d_{total}}$	3	2 ou 3	4	5.7	6.2	8.5	9

The position of the Fermi level as a function of the N_d number of electrons is shown for each alloy in Figure 7. The calculations of probability are made taking into account only the d states. One ignores the slight contribution coming from the association of the d and s states.
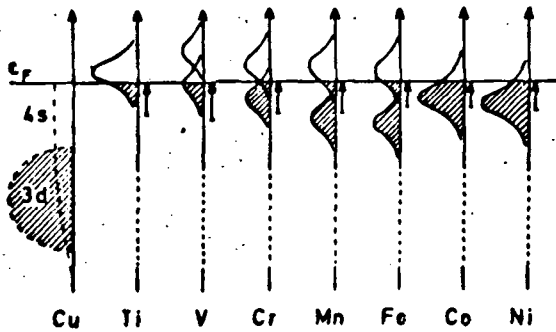
We will review the results of these calculations for different elements:

Fig. 7. Electron structures of the elements of transition in solution in copper. The hatched areas represent occupied states. The arrows show the quantities $E_m-\delta-E_F$.

-- <u>Titanium</u>: the quantity $E_m-\delta-E_F\sim 1$ eV is slightly higher for the half-width of a potential bound state. Then, it is not unreasonable to assume that all the d electrons participate in the formation of auto-ionizing states. Calculation of P_{CuTi}^{Ti} is then very simple and is shown by:

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$$P_{\underline{Cu}\,Ti}^{Ti} \sim \frac{\frac{1}{3} N_d^3}{\frac{1}{3} N^3}.$$

With $N_d = 3$ and a total number of electrons $N=4$, one finds $P_{\underline{Cu}Ti}^{Ti} \sim 0.4$ and $\chi_{CuTi} = 160$. This is a value which is very close to the ion constant $k_{exp} \sim 100 \pm 20$ (Fig. 8).

It is interesting to note the very direct manner by which this result has been obtained. The error from which it could be vitiated would eventually be provided from evaluation of N_d, but not by the width of the potential state. This then is a good test of the mechanism of proposed ionization.

-- Vanadium: One chooses the mean number of d electrons equal to 2.5 which figures in Table II. The potential d_+ state is then true for half full. As $E_m - \delta - E_F = 1.2$ eV is higher than Γ, one could also consider that all the d_+ electrons participate in populating the auto-ionizing states. Then one finds in taking the mean value of 2.5 electrons $P_{CuV}^V \sim 0.125$ and $\chi_{CuV} \sim 50$. This value is higher than the ion constant ($k_{exp} \sim 20$) (Fig. 8), but the calculation vitiates an error which arises from imprecision at which N_d is known.

-- Chromium: With four electrons, the d_+ state is almost full. One must have recourse this time to a complete calculation beginning with the parabolic approximation (expression 7). The details of the calculation are developed in the appendix. Here we will give the result $P_{CuCr}^{Cr} \sim 9 \times 10^{-2}$ and $\chi_{CuCr} \sim 35$. The last estimate is higher than the experimental value $k_{exp} \sim 15$, but always, is within acceptable limits (Fig. 8).

-- Manganese and iron: The d_+ state is full and cannot be used as Lorentz distribution for fixing its center according to the relationship to Fermi energy. The experimental studies of photo-emission [18] show well the presence of high density of states
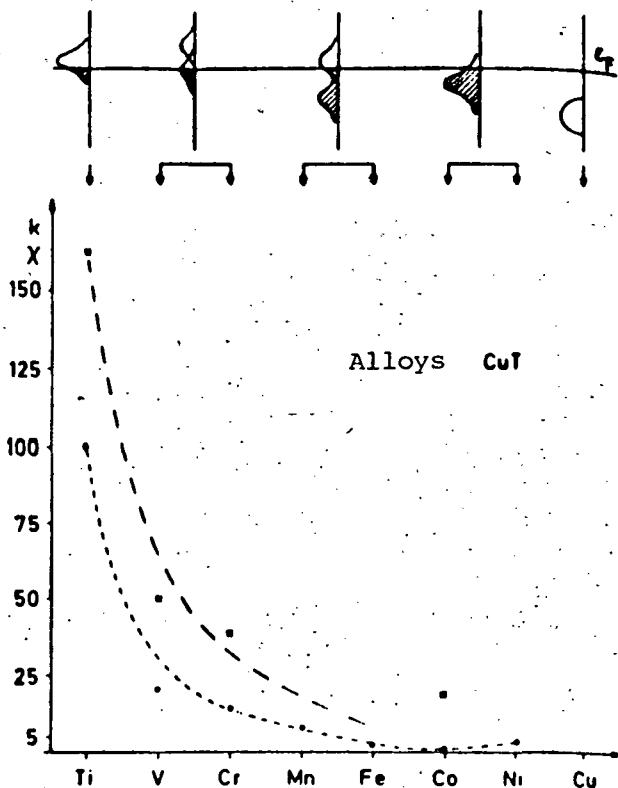
Fig. 8. Ion emission of elements of transition T in solution in copper. ⊙ measurements of ion constant k; × calculations of χ.

slightly below the Fermi level. It would seem that according to these experiments that one part of the d states of manganese, for example, is superimposed on the d states of the copper, but one cannot be precise as to the position of the resonance center. Calculation of the probability is, consequently, of no interest. Be that as it may, it is certain that the values of χ_{AB} of these elements must drop slightly in relation to the preceding from the fact of depression of the d states in the conduction band. This conclusion is supported by an experiment where one observes that the ion constant

$k_{CuMn}=7$ and $k_{CuFe}=1.8$ are weaker than those of the three first elements of the series (Fig. 8).

-- Cobalt: There is no decoupling of the d state which contains 8.5 electrons. Approximate calculation is the same for chromium: one uses a parabola (Fig. 5). This time, one finds $P_{CuCo}^{Co} \sim 1.5 \times 10^{-2}$ and $\chi_{CuCo} \sim 18$. This value is much higher than the ion constant $k_{exp} \sim 0.3$. One must always recall the particular case of this alloy which actually is not in solid solution at all if the concentration in cobalt is lower than 0.1% [26]. It is not magnetic in this case and it is with this hypothesis that one has obtained $\chi_{CuCo} \sim 18$. On the other hand, above a concentration of 0.1%, cobalt has a tendency to form small accumulations in which there is a magnetic state [26].

But the alloy studied has the concentration of 40%, and precipitates of cobalt have been observed (see the first section). Therefore, it is clear that the experimental result is not one which would give a good, solid solution.

--Nickel: The d state is not decoupled and is found almost filled with 9 electrons. This is a case where positioning of the resonance center in relation to the Fermi level is delicate. If one considers the Lorentz distribution of the center of resonance, it is located at 1.4 eV below the Fermi level. The photoemission experiments indicate 1.2 eV [18], which is in good agreement with the preceding value. The results are the following $P_{CuNi}^{Ni} \sim 1.5 \times 10^{-2}$ and $X_{CuNi} \sim 6$. This latter value is in very good agreement with $\overline{k_{exp}} \sim 3.5 \pm 0.5$ (Fig. 8).

In a general manner, one can say that in alloys based on copper (Fig. 8), the progression of the potential bound state across the Fermi level involves an increase in the probability of formation of auto-ionizing states measured by X_{AB} and comparable to that of ion emission; this shows a new justification for our ionization mechanism.

2.2.3. AlT Alloys.

One can show with a good approximation, the density of states of the conduction band of aluminum by a parabola [27] of 13 eV approximately in width. Shielding of the impurity of transition is assured by conduction electrons and by a crown of d electrons which are distributed on the potential bound state [17]. One would suppose that the conduction electrons which surround the atom of impurity are distributed on energy states in which the density is proportional to that of the conduction band of aluminum. The parabolic approximation is then maintained. There is no decoupling of the potential bound state in these alloys [17]. The situation is then
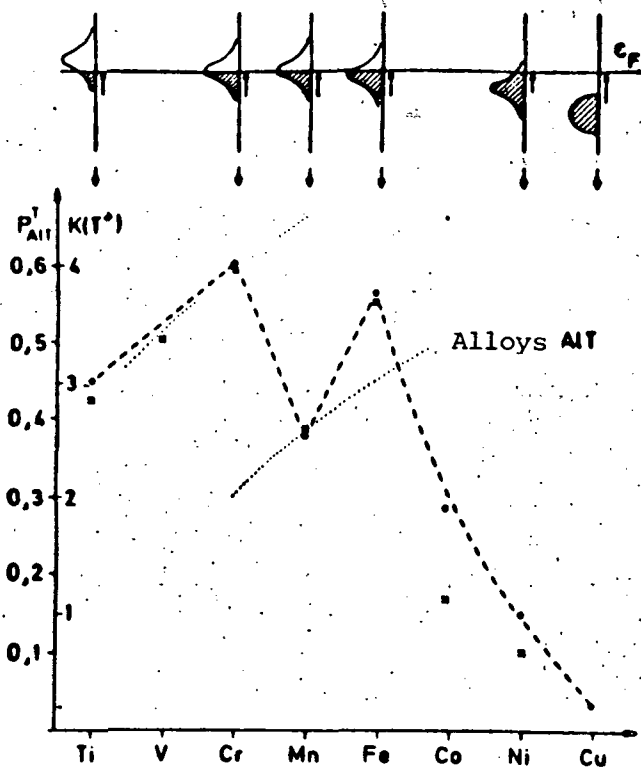
Fig. 9. Ion emission of elements of transition T in solution in aluminum: o ion yields $K(T^+)$ measured as a relative value (arbitrary unit); × calculations of probabilities P_{AlT}^T. The two dotted curves represent the calculated probabilities starting with the relationship $P \sim \left(1 - \frac{N_s}{N}\right)^3$ with N_s equal to 1 or 2.

TABLE III

		Ti	V	Cr	Mn	Fe	Co	Ni
	N total	4	5	6	7	8	9	10
electrons d	$\langle N_d \rangle$	3	4	5	5	6.6	7.25 (*)	8
electrons s	N_s	~1	1	1	2	1.4	1.75	2

much more simple in <u>Cu</u>T alloys. Experimentally, one observes an increase in ion emission of copper to iron, then a drop in the level of manganese, followed by a rise (Cr) and a decrease (V and Ti) (Fig. 9). We are going to show that the behavior is related to progression of the potential bound state across the Fermi level, as with the <u>Cu</u>T alloys, and to the number of electrons which it contains.

The width of the potential bound state of impurities of transition is slightly larger in the aluminum matrix than in that of copper [17]. We have chosen $2\Gamma = 2$ eV. The number of d electrons has been determined experimentally [28-29]. It is shown in Table III. One sees in the table that the number of s electrons is about one for Ti, V, Cr to 2 for Mn, Fe, Co, Ni. It is this statement that makes it possible to explain the oscillation of ion yields of titanium to iron.

[2] The mean value is interpolated between the values of iron and nickel.

-- <u>Titanium, vanadium, chromium, manganese, iron</u>: The bound
state is, at most, filled to half for iron. But the quantity
$E_m-\delta-E_F \sim 1$ eV is higher or on the same order as the half-width of
Γ. The situation is then identical with that of titanium and cop-
per and one can consider that all the d electrons participate in
the formation of auto-ionizing states. One could then write

$$P_{AIT}^T \sim \frac{\frac{1}{3} N_d^3}{\frac{1}{3} N^3}.$$

Overlapping of the conduction band and the potential state being
weak, one can neglect any contribution to auto-ionizing states
which would lead to associations d^2s or ds^2. In the same way,
one ignores the s^3 associations. The preceding relationship is
written

$$P_{AIT}^T \sim \left(1 - \frac{N_s}{N}\right)^3.$$

If N_s is nearly constant for a series of elements, the probability
of forming auto-ionizing states must increase when N increases,
that is to say, when the atomic number increases. The effect is
shown in figure 9 for $N_s=1$ and $N_s=2$. One sees that a minimum
for manganese appears clearly. The probabilities are calculated
(Fig. 9) for each element, beginning with the d number of elec-
trons which figures in Table III. These probabilities reproduce
very faithfully the variations of ion yields.

One should note that the expression $P_{AIT}^T=(N_d/N)^3$ certainly
represents a good approximation to the extent that N_d is well
known for titanium, vanadium and chromium. For iron, this ex-
pression slightly overestimates the probability because all the
electrons probably cannot be localized between the Fermi level
and the $E_m-\delta-E_F$ energy.

-- <u>Cobalt and nickel</u>: One must proceed here to calculation using a parabolic approximation of the density of the d states (calculation in the Appendix). In addition, one must have taken into account the contributions of d^2s and ds^2 which are not truly negligible due to the fact of important overlapping of the s band and the d state. Then, one finds $P_{AlCo}^{Co} \sim 0.14$ and $P_{AlNi}^{Ni} \sim 0.08$. These values reflect very well the spectacular drop of ion emission of cobalt and nickel.

-- <u>Copper</u>: The ring of d electrons is full, and the d states are dropped into the band of conductibility below the Fermi level. One does not have more information on the position of the center of resonance in order to calculate the probability of the formation of auto-ionizing states in copper. Meanwhile, one must expect that the lowering of the d states involves a drop in this probability as far as nickel is concerned; this is in agreement with the reduction in ion yield. Assuming that the ion emissions of copper and nickel are proportional to probabilities P_{AlCu}^{Cu} and P_{AlNi}^{Ni}, one finds

$$P_{AlCo}^{Cu} \sim \frac{1}{3,75} P_{AlNi}^{Ni} \sim 2,5 \times 10^{-2}.$$

This probability, higher than that which was calculated for pure copper $P_{Cu}^{Cu} \sim 2.5 \times 10^{-3}$ [4], could not have been obtained by participation of the d electrons in the formation of auto-ionizing states. One could then estimate that the center of resonance is located at 2 eV approximately below the Fermi level.

3. Discussion of the interpretation.

It stands out from our study that, for an element in solution, a very clear correlation exists between electron density close to the Fermi level and the ion emission yield.

On the other hand, residual resistivity of the alloys examined depends equally on electron density at the Fermi level.

Also, is it natural to observe a certain relationship between the evolutions of residual resistivity of a series of alloys with the same matrix and ion emissions. There always exist differences which occur, due to the fact that electrons which participate in the formation of auto-ionizing states are retained in a band of energy which is relatively large (approximately 1 eV) whereas those which cause resistive effects are localized at the Fermi level itself.

Inasmuch as the fraction of electrons concerned in the formation of auto-ionizing states and the electron density of the Fermi level progress simultaneously, one can witness a parallel evolution of the curves of resistivity [17] and ion emission. This is roughly the situation of elements of transition at the end of the series in most of the matrices used, and it is the case in alloys based on nickel where chromium gives a particularly spectacular effect. On the other hand, for the elements at the beginning of the series, in solution in normal metal, resistivity is low because the electron density at the Fermi level decreases [17], whereas ion emission is often very high (for example, titanium and vanadium in copper). All the same, for the elements in the middle of the series, the minimum ion emission of manganese in aluminum is not found on the curve of resistivity [17] and the double hump of resistivity of CuT alloys [17] was not observed in ion emission.

Our calculations take into account the general course of the phenomena and, in particular, the peculiarities of emissions of chromium in nickel and elements of transition in aluminum (Ti, Cr, Mn, Fe) but they are often very approximate.

One could consider improving the agreement with experiments by adjusting, for example at least the width of the potential state in the CuT alloys where again a fraction of electrons

would be slightly modified which participate in the formation of auto-ionizing states in $\underline{\text{NiT}}$ alloys. That amounts, in a way, considering that the calculator probability χ_{AB} is comparable to the ion constant. But this method of operation has a limited interest because one must not lose sight of the fact that up until now, we have not been able to take into account the eventual variation of $F_d(v)$ in which the effect naturally would change the probabilities of ionization. We will then restrict ourselves to taking values generally admissible in literature in spite of their lack of precision.

Our model describes too briefly the exit of the atom which would make it possible to calculate probability $F_d(v)$. On the other hand, Joyes and Toulouse [30], going from the idea that electrons delocalized close to the Fermi level cannot easily follow the atom in its movement, have shown that a certain probability exists for an electron deficiency on the d layer of the atom once the latter has left the metal. Then, one has there the mechanism of formation of the d hole which can serve as the basis for calculation $F_d(v)$. However, these authors have not taken into account electrons which could form excited states and compare "ionization of the d level" to ionization of the atom. Then, one finds the existence of another interpretation of ion emission in which the probability of ionization would equally follow an evolution similar to that of residual resistivity, taking into account the fact that the magnetic state of an ejected atom could be different from that of an immobile atom at a site. Also, decoupling of the magnetic state of chromium and manganese in copper [17] would not be maintained on an atom in motion which would lead to a stronger probability of ionization than could occur from the large residual resistivity of these impurities in a nonmagnetic state (one no longer observes a double hump in this case). On the contrary, the atoms of mangenese coming from an aluminum matrix could take on a magnetic state which would give slight resistivity and would lower emission of this element in relation to emissions of their close neighbors, chromium and iron (Fig. 9).

This interpretation is attractive, but it remains qualitative because the amplidute of the effects have not been calculated. In other words, it is difficult to interpret   **from**   this model, evolution of ion emissions of alloys on a base of copper (Fig. 8) and, in particular, it is difficult to prove the strong possibilities of ionization of titanium and vanadium.

It is not just that if one limits the model to the formation of the d hole, $F_d(v)$ could vary with the solute and the matrix being considered.One still has to find out if (and in which cases) the amplitude of variations is sufficient to have a significant effect on the probabilities of ionization.

Nevertheless, it is clear that if a theory similar to that of Joyes and Toulouse could be carried out to the numerical conclusions and if one takes into account all the electrons, it would make it possible at least to rate the validity of our model and perhaps to prove such hypotheses as that of the conservation of the baryonic center of energy of electrons which form an auto-ionizing state during transition which causes exit from the metal.

Let us note again that this transition has been formulated by Schroeer[31] within the framework of an adiabatic approximation. In treating the exit of the atom as a perturbation and in arbitrarily choosing a solution with two adjustable parameters for Hamiltonian interaction, one arrives at the expression of probability of ionization as:

$$P_1 = \left(\frac{A}{I-\Phi}\right)^2\left[\frac{\hbar v}{a(I-\Phi)}\right]^n.$$

A is the energy of sublimation, I is the energy of ionization, Φ is the work of exit, h is Planck's constant. The parameters a and n are adjustable.

The parameter *A* varies slightly in the series of elements of
3d transition (with the exception of manganese) and the variations
of ionic yield essentially carry the differences $I - \Phi$. These dif-
ferences have a tendency to diminish when one examines the series
of copper to titanium of the type where the ion yields forseen
increase from the end to the beginning of the series. Effectively,
it is that which one observes qualitatively for pure metals, but
the relationship proposed by Schroeer gives results which often
diverge from experimental results. It has been remarked that,
by playing with the end parameter, one cannot reach a correction
of these divergences, but one simply modifies the amplitude of
variation of the function. (Based on the measurements of Beske,
Schroeer has deduced from them $n \sim 3$ and $a \sim 1 \overset{o}{A}$.)

The same formula can be used to calculate ion constants of al-
loys and in all cases, it gives a slight increase of copper in
titanium without taking into account the also-marked effects such
as those noted in the CuT, NiT or AlT alloys.

The process of ion emission which we have proposed and which
is well supported by experiments is in a narrow relationship to
the local electron structure of the atoms. Therefore, it seems
that ion emission can be a new source of information for elec-
tron properties of impurities in alloys.

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APPENDIX

In using the notations of figure 10:

ε', ε'' energy of electrons of an atom when $x \leq x_c$

ε_F Fermi energy

$n(\varepsilon)$ electron density of the atom in x_c

$$U = E - \delta \quad \text{et} \quad U_m = E_m - \delta$$
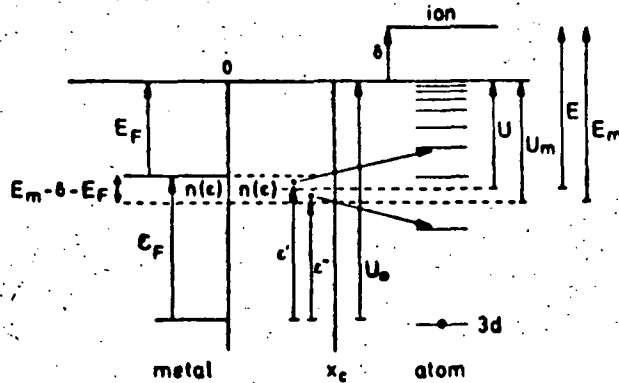
One shows [4] that the probabilities of formation of auto-ionizing states are written:

$$P(U_m - E_F) = \frac{\displaystyle\int_{E_f}^{U_m} T[2(U_0 - U)]\,dU}{\displaystyle\int_{E_r}^{U_0} T[2(U_0 - U)]\,dU}$$

with   (A.1)

$$T[2(U_0 - U)] = \int_0^{\varepsilon_F} n(\varepsilon')\, n[2(U_0 - U) - \varepsilon']\,d\varepsilon'$$

when a process of auto-ionization between two electrons is put into play, and:

$$P(U_m - E_F) = \frac{\displaystyle\int_{E_f}^{U_m} N[3(U_0 - U)]\,dU}{\displaystyle\int_{E_F}^{U_0} N[3(U_0 - U)]\,dU}$$ (A.2)

with

$$N[3(U_0 - U)] = \int_0^{\varepsilon_F} n(\varepsilon') \, T[3(U_0 - U) - \varepsilon'] \, d\varepsilon'$$

when the process involves three electrons.

In making changes in the variable $X=2(U_0-U)$ and taking into account the fact that $U_0-E_F=\varepsilon_F$, one finds that the denominator of the expression (A.1) is written:

$$\frac{1}{2}\int_0^{2\varepsilon_F} T(X) \, dX = \frac{1}{2}\int_0^{\varepsilon_F} n(\varepsilon')\left[\int_0^{2\varepsilon_F} n(X - \varepsilon') \, dX\right] d\varepsilon' \, .$$

But, $n(\varepsilon)=0$ for $-\varepsilon'<\varepsilon<0$ and for $\varepsilon_F<\varepsilon<2\varepsilon_F-\varepsilon'$ (ε' is at the maximum equal to ε_F), and therefore:

$$\int_0^{2\varepsilon_F} n(X - \varepsilon') \, dX = \int_{-\varepsilon'}^{2\varepsilon_F-\varepsilon'} n(\varepsilon) \, d\varepsilon = \int_0^{\varepsilon_F} n(\varepsilon) \, d\varepsilon = N_0$$

where N_0 is the number of d+s electrons of the atom. Finally:

$$\int_{E_F}^{U_0} T[2(U_0 - U)] \, dU = \frac{1}{2} N_0^2 \, .$$

One obtains a similar result for the denominator of the (A.2) expression, being:

$$\int_{E_F}^{U_0} N[3(U_0 - U)] \, dU = \frac{1}{3} N_0^3 \, .$$

For carrying out the calculations, it is convenient to introduce the variables $U-E_F=A$, $U_m-E_F=A_m$ and $U_0-E_F=\Delta$. If (a, b) is one of the intervals of variation of A so that $a \leq A \leq b$, calculation of the probabilities is brought back to that of integrals:

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Being: $$R_{ab} = \int_a^x T_{ab}\, dA \quad \text{or} \quad R_{ab}(x) = \int_a^x N_{ab}\, dA.$$

$$P(A_m) = \frac{R_{0,A_m}(A_m)}{R_{0,A}(A)} \tag{A.3}$$

with $$R_{0,A}(A) = \tfrac{1}{2} N_0^2 \quad \text{or} \quad \tfrac{1}{3} N_0^3.$$

The approximation used in the calculations consists of taking electron density $n(\varepsilon)$ of atoms in x_c identical to that which one finds in the neighborhood of the Fermi level around the atom, in the metal or in the alloy. In practice, this approximation is applicable to a width equal to 2 or 3 times A_m (being 2 eV maximum) as the structure of the auto-ionizing states carries two or three electrons. If it is deemed necessary to pursue the calculations to this limit, one has no other recourse but to take this same approximation because one ignores exactly the electron density of the atom in x_c, but the results will be less valid then.

1. Electron density α is constant; the auto-ionizing states formed by two electrons (Fig. 11b). This approximation has been used for pure metals [4], manganese, vanadium, titanium, for which $A_m < \Delta/2$, being:

$$P(A_m) = \frac{\alpha^2 A_m^2}{\tfrac{1}{2} N_0^2}. \tag{A.4}$$

2. Density of states A and two constants α and α' ($\alpha' < \alpha$); auto-ionizing states formed by two electrons (Fig. 11a and c). This approximation has been used for pure chromium [4] ($A_m < A'/2$) being:

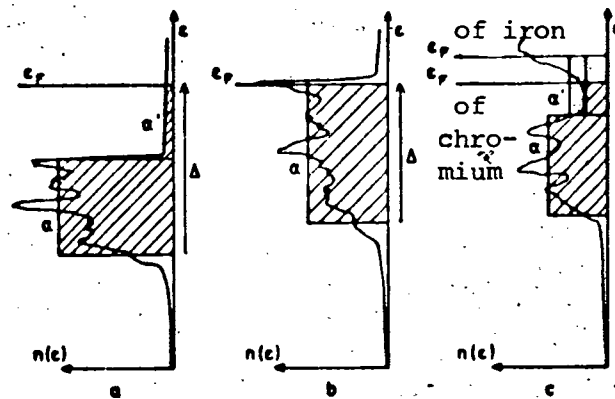$$P(A_m) = \frac{\alpha'^2 A_m^2}{\tfrac{1}{2} N_0^2} \tag{A.5}$$

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Fig. 11. The approximate forms of density of the states of pure metals used for calculating the probabilities of formation of auto-ionizing states: a) case of copper; b) case of nickel, cobalt, titanium, vanadium and manganese; c) case of chromium (hatched zone) and of iron (zone with dots added).

and for pure copper [4] where

$$\frac{A'}{2} < \frac{A}{m} < A'$$

$$P(A_m) = \frac{\alpha'^2\left(\frac{A'}{2}\right)^2 + \left(A_m - \frac{A'}{2}\right)\left[2\,\alpha\alpha'\left(A_m - \frac{A'}{2}\right) - \alpha'^2\left(A_m - \frac{3}{2}A'\right)\right]}{\frac{1}{2}\,N_0^2} \qquad (A.6)$$

3. Electron density constant α; the auto-ionizing states formed by three electrons (Fig. 11b). The approximation used for pure cobalt and nickel [4], for which $A_m < A/3$ is:

$$P(A_m) = \frac{\frac{3}{2}\,\alpha^3\,A_m^3}{\frac{1}{3}\,N_0^3}. \qquad (A.7)$$

4. The density of states A of two constants α and α' ($\alpha' < \alpha$); the auto-ionizing states formed by three electrons (Fig. 11c).

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$$n(\varepsilon) = \alpha \qquad 0 \leqslant \varepsilon \leqslant \varepsilon'$$
$$n(\varepsilon) = \alpha \qquad \varepsilon' \leqslant \varepsilon \leqslant \Delta$$
$$n(\varepsilon) = 0 \qquad \varepsilon < 0; \ \varepsilon > \Delta .$$

The calculation is made for the following order of increasing values of A:

$$0, \ \frac{A'}{3}, \ \frac{2A'}{3}, \ \frac{\Delta}{3}, \ A', \ \frac{\Delta + A'}{3}, \ \frac{\Delta + 2A'}{3}, \ \frac{2\Delta}{3}, \ \frac{2\Delta + A'}{3}, \ \Delta .$$

Interval $a < A < b$	$R_{ab}(x)$
$0; \dfrac{A'}{3}$	$\dfrac{3}{2} \alpha'^3 x^3$

$$\frac{A'}{2}; \frac{2A'}{3} \qquad 3\left(x - \frac{A'}{3}\right)\left\{\frac{3}{2}\alpha\alpha'^2\left(x - \frac{A'}{3}\right)^2 + \frac{\alpha'^3}{2}\left[xA' - 2\left(x - \frac{A'}{3}\right)^2\right]\right\}$$

$$\frac{2A'}{3}; \frac{\Delta}{3} \qquad 3\left(x - \frac{2A'}{3}\right)\left\{\frac{3}{2}\alpha^2\alpha'\left(x - \frac{2A'}{3}\right)^2 + \frac{\alpha\alpha'^2}{2}\left(7A'x - \frac{7}{3}A'^2 - 3x^2\right) +$$
$$+ \frac{\alpha'^3}{2}\left[\left(x - \frac{2A'}{3}\right)^2 - A'(x - A')\right]\right\}$$

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$$\frac{\Delta}{3}; A' \qquad 3\left(x - \frac{\Delta}{3}\right)\left\{\frac{\alpha^2\alpha'}{2}\left[3\left(x - \frac{\Delta}{3}\right)^2 + (3x - 2A')(\Delta - 2A')\right] +$$
$$+ \frac{\alpha\alpha'^2}{2}\left[\left(x + \frac{\Delta}{3}\right)(\Delta + 9A' - 6x) + 2\Delta x - \Delta^2 - 7A'^2\right]$$
$$+ \frac{\alpha'^3}{2}\left[\left(x - \frac{\Delta}{3}\right)^2 + (A' - x)(3A' - \Delta)\right]\right\}$$

$$A'; \frac{\Delta + A'}{3} \qquad 3(x - A')\left\{\frac{\alpha^3}{2}(x - A')^2 + \frac{\alpha^2\alpha'}{2}A'(3x - 2A') +$$
$$+ \alpha\alpha'^2\left[A'^2 - \frac{3}{2}(x - A')^2 - \frac{1}{2}(\Delta - 3A')(\Delta - 3x)\right]\right\}$$

$$\frac{\Delta + A'}{3}; \frac{\Delta + 2A'}{3} \qquad 3\left(x - \frac{\Delta + A'}{3}\right)\left\{\frac{\alpha^3}{18}\left[(3x - \Delta - A')^2 + 9(x - A')(\Delta - 2A')\right] +$$
$$+ \frac{\alpha^2\alpha'}{6}\left[2(\Delta - 3x)^2 + A'(7\Delta - 3x - 10A')\right]$$
$$+ \frac{\alpha\alpha'^2}{6}\left[(\Delta - 3x)^2 + A'(5\Delta - 15x + 7A')\right]\right\}$$

$$\frac{\Delta + 2A'}{3}; \frac{2\Delta}{3} \qquad 3\left(x - \frac{\Delta + 2A'}{3}\right)\left\{\alpha^3\left[\frac{1}{2}(\Delta + A')(x + A') - A'(x + \Delta) - \left(x - \frac{\Delta + 2A'}{3}\right)^2\right] +$$
$$+ \frac{\alpha^2\alpha'}{2}A'(3\Delta - 3x - A')\right\}$$

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$$\frac{2\Delta}{3}; \frac{\Delta+A'}{3} \qquad 3\left(x-\frac{2\Delta}{3}\right)\left\{\alpha^3\left[\frac{1}{2}(\Delta+A')(\Delta-A'+3x)-\Delta(A'+2x)-\left(x-\frac{2\Delta}{3}\right)^2\right]+\right.$$

$$\left.+\frac{\alpha^2\alpha'}{6}\left[(2\Delta-3x)^2+3A'(2\Delta-3x+A')\right]\right\}$$

$$\frac{2\Delta+A'}{3}; \Delta \qquad \frac{3}{2}\alpha^3\left(x-\frac{2\Delta+A'}{3}\right)\left[(\Delta-x)(\Delta-A')+\left(\frac{2\Delta+A'}{3}-x\right)^2\right].$$

This approximation is applied to pure iron [4] where $A_m < 2A'/3$

$$P(A_m) = \frac{\frac{\alpha'^3}{18}A'^3 + 3\left(A_m-\frac{A'}{3}\right)\left\{\frac{3}{2}\alpha\alpha'^2\left(A_m-\frac{A'}{3}\right)^2+\frac{\alpha'^3}{2}\left[A_m A'-2\left(A_m-\frac{A'}{3}\right)^2\right]\right\}}{\frac{1}{3}N^3} \quad (A.8)$$

5. Electron density in a potential bound state. The Lorentzian electron density is approximated by a parabola. With the notations used on figure 12, the equation of this parabola is written:

$$\delta n(\varepsilon) = \alpha\varepsilon(a-\varepsilon) \qquad \text{for} \quad 0 < \varepsilon < \Delta$$
$$\delta n(\varepsilon) = 0 \qquad \text{for} \quad \varepsilon < 0; \ \varepsilon > \Delta.$$

The parameters a and α are adjusted for each particular case. One always arranges to conserve the value of the density of states of the center of resonance, being $\frac{2(2l+1)}{\pi\Gamma}$ if there is no decoupling and $\frac{2l+1}{\pi\Gamma}$ if there is decoupling. This imposes the following relationship:

$$\frac{\alpha a^2}{4} = \frac{2(2l+1)}{\pi\Gamma} \qquad \text{when there is no decoupling and}$$

$$\frac{\alpha a^2}{4} = \frac{2l+1}{\pi\Gamma} \qquad \text{when there is decoupling.}$$

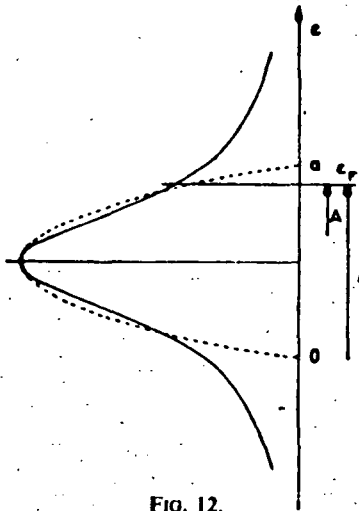The auto-ionizing states formed by three electrons: one assumes $k=3(\Delta-A)$.

Fig. 12.

Interval

$a < A < b$ $\qquad\qquad\qquad\qquad\qquad N_{ab}(k)$

$0; \dfrac{\Delta}{3}$

$$\alpha^2 \left\{ -2\Delta^4(a-\Delta)\left(\frac{\Delta^2}{5}-\frac{a^2}{3}\right)(k-\Delta) - \frac{\Delta^3}{3}\left(\frac{a^3}{3}+a^2\Delta-\frac{19}{15}a\Delta^2+\frac{\Delta^3}{5}\right)(k-\Delta)^2 + \right.$$

$$+\frac{\Delta^2}{3}\left(\frac{\Delta^3}{15}-\frac{\Delta^2 a}{2}+\Delta a^2-\frac{a^3}{2}\right)(k-\Delta)^3 + \frac{\Delta}{12}\left(\frac{\Delta^3}{3}-2\Delta^2 a+\frac{3}{2}\Delta a^2+\frac{a^3}{2}\right)(k-\Delta)^4$$

$$+\frac{1}{30}\left(\frac{a^3}{4}-\frac{3a^2\Delta}{2}+\frac{2}{3}\Delta^3\right)(k-\Delta)^5 + \frac{1}{180}\left(-\Delta^2+3\Delta a-\frac{3a^2}{2}\right)(k-\Delta)^6$$

$$+\frac{1}{630}\left(\frac{3a}{2}-\Delta\right)(k-\Delta)^7 - \frac{(k-\Delta)^8}{5\,040} + \frac{2\Delta^5}{3}k(a-k)\left(\frac{\Delta}{3}-\frac{2a}{5}\right)$$

$$\left.+\frac{4\Delta^5}{3}(2k-a)\left(\frac{a^2}{5}-\frac{a\Delta}{3}+\frac{\Delta^2}{7}\right) - 4\Delta^6\left(\frac{a^2}{9}-\frac{6a\Delta}{35}+\frac{\Delta^2}{15}\right)\right\};$$

$\dfrac{\Delta}{3}; \dfrac{2\Delta}{3}$

$$\alpha^2 \left\{ \Delta^4 k(a-k)\left(\frac{a^2}{4}-\frac{a\Delta}{15}-\frac{\Delta^2}{9}\right) + \Delta^5(2k-a)\left(\frac{a^2}{5}-\frac{\Delta^2}{42}-\frac{a\Delta}{36}\right) + \frac{\Delta^6}{2}\left(\frac{\Delta^2}{60}+\frac{a\Delta}{35}-\frac{a^2}{15}\right) + \right.$$

$$+a\Delta^3\left(\frac{\Delta^2}{5}-\frac{a^2}{3}\right)k^2 + \frac{\Delta^2}{3}\left(\frac{a^3}{2}+a^2\Delta-\frac{a\Delta^2}{2}-\frac{2\Delta^3}{5}\right)k^3 + \frac{\Delta^2}{12}(\Delta^2-2a^2)k^4$$

$$-\frac{1}{30}\left(\frac{a^3}{4}-a\Delta^2+\frac{2\Delta^3}{3}\right)k^5 + \frac{a^2 k^6}{120} - \frac{ak^7}{420} + \frac{k^8}{5\,040} - \frac{\Delta a^2}{24}(a-\Delta)(k-\Delta)^4$$

$$+\frac{a}{30}\left(-\Delta^2-\frac{a^2}{4}+\frac{3}{2}a\Delta\right)(k-\Delta)^5 + \frac{1}{180}\left(\Delta^2-3a\Delta+\frac{3}{2}a^2\right)(k-\Delta)^6$$

$$\left.-\frac{1}{630}\left(\frac{3a}{2}-\Delta\right)(k-\Delta)^7 + \frac{(k-\Delta)^8}{5\,040}\right\}$$

$\dfrac{2\Delta}{3}; \Delta$

$$\alpha^2 \left\{ \frac{a^3}{120}k^5 - \frac{a^2}{120}k^6 + \frac{a}{420}k^7 - \frac{k^8}{5\,040}\right\}.$$

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Calculation of $R_{ab}(x)$. One assumes that $X=3(\Delta-x)$.

Interval

$a < \Lambda_m < b$	$R_{ab}(x)$

$0;\dfrac{\Delta}{3}$

$$\alpha^3 \left\{ +\frac{\Delta^4}{3}(a-\Delta)\left(\frac{\Delta^2}{5}-\frac{a^2}{3}\right)(X-\Delta)^2 + \frac{\Delta^3}{18}\left(\frac{a^3}{3}+a^2\Delta-\frac{19\,a\Delta^2}{15}+\frac{\Delta^3}{5}\right)(X-\Delta)^3 - \right.$$

$$-\frac{\Delta^2}{36}\left(\frac{\Delta^3}{15}-\frac{\Delta^2 a}{2}+\Delta a^2-\frac{a^3}{2}\right)(X-\Delta)^4 - \frac{\Delta}{180}-\left(\frac{\Delta^3}{3}-2\Delta^2 a+\frac{3}{2}\Delta a^2+\frac{a^3}{2}\right)(X-\Delta)^5$$

$$-\frac{1}{540}\left(\frac{a^3}{4}-\frac{3\,a^2\Delta}{2}+\frac{2}{3}\Delta^3\right)(X-\Delta)^6-\frac{1}{3\,780}\left(-\Delta^2+3\,\Delta a-\frac{3}{2}a^2\right)(X-\Delta)^7$$

$$-\frac{1}{15\,120}\left(\frac{3}{2}a-\Delta\right)(X-\Delta)^8+\frac{(X-\Delta)^9}{136\,080}+\frac{2}{27}\Delta^5\left(\frac{\Delta}{3}-\frac{2a}{5}\right)X^3-\frac{2}{9}\Delta^5\left(\frac{2\Delta^2}{7}+\frac{a^2}{5}-\frac{a\Delta}{2}\right)X^2 \qquad \underline{/259}$$

$$\left.+\frac{4\Delta^5}{45}\left(\Delta^3-\frac{13\,\Delta a}{7}+a^3\right)X+\frac{\Delta^6}{135}\left(-\frac{86}{9}\Delta^3+19\,\Delta^2 a-\frac{6}{7}\Delta a^2-10\,a^3\right)\right\} ;$$

$\dfrac{\Delta}{3};\dfrac{2\Delta}{3}$

$$\alpha^3\left\{+\frac{\Delta^6}{280}\left(-\frac{53\Delta^3}{81}+\frac{589\Delta^2 a}{108}-9\,\Delta a^2+\frac{77\,a^3}{18}\right)+\frac{\Delta^5}{90}\left(2\,a^3-\frac{8\,a\Delta^2}{7}-\frac{\Delta^3}{4}\right)X+\right.$$

$$+\frac{\Delta^4}{18}\left(\frac{\Delta^3}{7}+\frac{\Delta^2 a}{2}-\frac{\Delta a^2}{5}-\frac{3\,a^3}{4}\right)X^2+\frac{\Delta^3}{9}\left(\frac{a^3}{3}+\frac{\Delta a^2}{4}-\frac{4\,\Delta^2 a}{15}-\frac{\Delta^3}{9}\right)X^3$$

$$-\frac{\Delta^2}{36}\left(\frac{a^3}{2}+a^2\Delta-\frac{a\Delta^2}{2}-\frac{2\,\Delta^3}{5}\right)X^4-\frac{\Delta^2}{180}(\Delta^2-2\,a^2)X^5+\frac{1}{540}\left(\frac{a^3}{4}-a\Delta^2+\frac{2}{3}\Delta^3\right)X^6$$

$$-\frac{a^2 X^7}{2\,520}+\frac{aX^8}{10\,080}-\frac{X^9}{136\,080}+\frac{\Delta a^2}{360}(a-\Delta)(X-\Delta)^5-\frac{a}{540}\left(\frac{3}{2}a\Delta-\Delta^2-\frac{a^2}{4}\right)(X-\Delta)^6$$

$$\left.-\frac{1}{3\,780}\left(\Delta^2-3\,a\Delta+\frac{3}{2}a^2\right)(X-\Delta)^7+\frac{1}{15\,120}\left(\frac{3\,a}{2}-\Delta\right)(X-\Delta)^8-\frac{(X-\Delta)^9}{136\,080}\right\} ;$$

$\dfrac{2\Delta}{3};\Delta$

$$\alpha^3\left\{+\frac{\Delta^6}{360}\left(\frac{a^3}{6}-\frac{a^2\Delta}{7}+\frac{a\Delta^2}{28}-\frac{\Delta^3}{378}\right)-\frac{X^6}{360}\left(\frac{a^3}{6}-\frac{a^2 X}{7}+\frac{aX^2}{28}-\frac{X^3}{378}\right)\right\} .$$

A particular case: $a=\Delta$, $X=3(\Delta-x)$.

Interval

$a < \Lambda_m < b$	$R_{ab}(x)$

$0;\dfrac{\Delta}{3}$

$$\frac{\alpha^3}{135}\left\{2\,\Delta^6(X-\Delta)^3-\frac{\Delta^5}{4}(X-\Delta)^4-\frac{\Delta^4}{4}(X-\Delta)^5+\frac{7\,\Delta^3}{48}(X-\Delta)^6-\frac{\Delta^2}{56}(X-\Delta)^7-\frac{\Delta}{224}(X-\Delta)^8+\right.$$

$$\left.+\frac{(X-\Delta)^9}{1\,008}-\frac{2\,\Delta^6 X^3}{3}+\frac{3}{7}\Delta^7 X^2+\frac{12}{7}\Delta^8 X-\frac{89\,\Delta^9}{63}\right\} ;$$

$\dfrac{\Delta}{3};\dfrac{2\Delta}{3}$

$$\frac{\alpha^3}{180}\left\{-\frac{5\,\Delta^9}{72}+\frac{17\,\Delta^8 X}{14}-\frac{43}{14}\Delta^7 X^2+\frac{37}{9}\Delta^6 X^3+2\,\Delta^5 X^4+\Delta^4 X^5-\frac{\Delta^3 X^6}{36}-\frac{\Delta^2 X^7}{14}+\frac{\Delta X^8}{56}-\right.$$

$$\left.-\frac{X^9}{756}-\frac{\Delta^3(X-\Delta)^6}{12}+\frac{\Delta^2}{42}(X-\Delta)^7+\frac{\Delta}{168}(X-\Delta)^8-\frac{(X-\Delta)^9}{756}\right\} ;$$

$\dfrac{2\Delta}{3};\Delta$

$$\frac{\alpha^3}{360}\left\{\frac{43\,\Delta^9}{756}-X^6\left(\frac{\Delta^3}{6}-\frac{\Delta^2}{7}X+\frac{\Delta}{28}X^2-\frac{X^3}{378}\right)\right\} .$$

a) Application to CuT alloys. The width of the potential
state is $2\Gamma=1$ eV.

-- Chromium: The decoupled potential state d_+ contains 4 elec-
trons. It has an excellent approximation for the parabola $a=2\sqrt{2}\Gamma$
(Fig. 13), which gives a width at mid-height 2Γ equal to that of
the Lorentzian.

The parameters are the following:

$$a \sim 1.4 \text{ eV}$$

$$\alpha = 6.3 \frac{\text{electrons}}{\text{atom (eV)}^3}.$$

This approximation has the large advantage of making it possible
to use the particular case $a=\Delta=1.4$ eV.

One could have an order of magnitude very satisfactory for
probability, noting that $A_m=1.1\sim 2\Delta/3$. Assume

$$P_{\underline{Cu}Cr}^{Cr} = \frac{R_{0,\Delta/3}(\Delta/3) + R_{\Delta/3,2\Delta/3}(2\,\Delta/3)}{\frac{1}{3}\,6^3}.$$

With

$$R_{0,\Delta/3}\,\frac{\Delta}{3} = \frac{43}{360 \times 756}\alpha^3\,\Delta^9, \qquad R_{\Delta/3,2\Delta/3}\left(\frac{2\Delta}{3}\right) = \frac{334}{360 \times 756}\alpha^3\,\Delta^9. \tag{A.9}$$

One finds then
$$P_{\underline{Cu}Cr}^{Cr} \sim 9 \times 10^{-2}.$$

-- Cobalt: There is no decoupling. The potential state
contains 8.5 electrons, of which 3.5 are above the center of re-
sonance. One calculates the parameters of the parabola by main-
taining this number of electrons above the center of resonance;
assume:

$$a = \Delta = 1.65 \text{ eV}, \qquad \alpha = 9.4 \frac{\text{electrons}}{\text{atom (eV)}^3}.$$
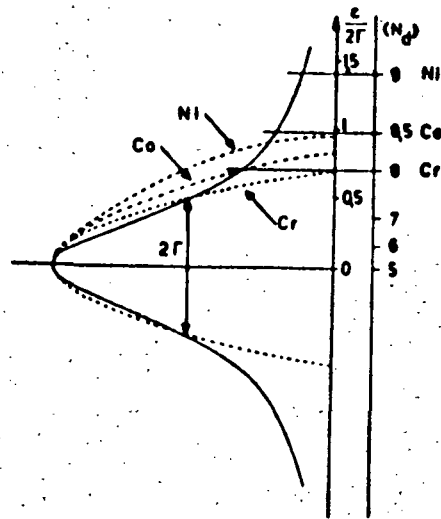
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Fig. 13. Parabolic approximations used as a function of
the degree of occupation of the potential state. If the
d state is decoupled, it must be divided by double the
number of $\langle N_d \rangle$ which is indicated on the figure.

In this approximation, a is slightly below the Fermi level, about
0.175 eV (Fig. 13). The value of $A_m = 0.7$ eV must then decrease
from 0.175 eV. It stops at 0.525 eV.

When 0.525 eV$\sim\Delta.3$, it will be

$$P_{\underline{Cu}Co}^{Co} \sim \frac{R_{0,\Delta/3}(\Delta/3)}{\frac{1}{3}9^3}$$

with $R_{0,\Delta/3}(\Delta/3)$ given by expression (A.9). Assume

$$P_{\underline{Cu}Co}^{Co} \sim 4.5 \times 10^{-2}.$$

The approximation used subtracts a certain number of auto-
ionizing states. But on the other hand, the density of the
states in the parabola is higher than in the Lorentzian. Then,
there is a partial compensation and it is probable that the er-
ror committed is not too important.

--<u>Nickel</u>: The potential state contains 9 electrons, four of which are above the center of resonance. One uses the same type of parabolic approximation as for cobalt, which retains 4 electrons above the center of resonance. The parameters are the following:

$$a = \Delta = 1.9 \text{ eV}, \qquad \alpha = 7\frac{\text{electrons}}{\text{atom} \ (\text{eV})^3}.$$

The quantity $A_m = 0.85$ must decrease in the case of 0.4 eV. It stops then at 0.45 eV. $0.45 < \Delta/3$; the calculation must then be conducted starting from the expression of $R_{0,\Delta/3}(x)$ in a particular case $a = \Delta$: One finds

$$P_{\underline{Cu}Ni}^{Ni} \sim 15 \times 10^{-2}.$$

b) <u>Application to AlT alloys</u>. There are, respectively, 7.25 and 8 d electrons for cobalt and nickel. The parabolic approximation with $a = 2\sqrt{2}\Gamma$ agrees perfectly then (Fig. 13). It has selected $\Gamma = 1$ eV, in which $a \sim 2.8$ eV and $\alpha = 5/\pi \sim 1.6$ electron/atom (eV)^3. Otherwise, one considers the two electrons which the atom loses at the band of conductibility of aluminum. In always assuming that the density of the states is parabolic around the impurity, one is led to an electron density at the Fermi level $n_s = 0.22$ electron/atom eV. One would assume this density to be constant at 2 or 3 eV, in order to carry out the calculation:

$$P_{\underline{Al}T}^T = \frac{R_{d^3} + R_{s^3} + R_{d^2 s} + R_{d s^2}}{\frac{4}{3} N^3}.$$

-- For cobalt $A - 2.28$ eV$< a$ and $A_m = 0.8$ eV is very slightly higher at $A/3$.

-- For nickel, $a = \Delta = 2.8$ eV and $A_m = 1.06$ eV$> \frac{A}{3}$. R_{d^2}[illegible] is calculated for $\frac{A}{3} < A_m < \frac{2A}{3}$.

$$R_0 = \frac{3}{2} n_a^2 A_m^3$$

$$R_{01} = n_a^2 a A^2 \left\{ \frac{A^2}{12}\left(\frac{3a}{2} + \frac{17A}{15}\right) + A\left(A_m - \frac{A}{3}\right)\left(a - \frac{3A}{4}\right) + \frac{9}{2}\left(A_m - \frac{A}{2}\right)^2\left(\frac{a}{2} - \frac{A}{3}\right) \right\}$$

$$R_{02} = n_a a^3 \left\{ \frac{A^3}{3}\left(\frac{A^2}{6} - \frac{Aa}{5} + \frac{a^2}{3}\right) + A^4\left(A_m - \frac{A}{3}\right)\left(\frac{A^2}{4} + \frac{1}{4}a^2 - aA\right) + \right.$$
$$\left. + \frac{1}{60}(2A - 3A_m)^2\left[\frac{a^2}{2} - \frac{a}{3}(2A - 3A_m) + \frac{(2A - 3A_m)^2}{51}\right] \right\}$$

One finds for nickel, $P_{AlNi}^{Ni} - 8 \times 10^3$ and for cobalt $P_{AlCo}^{Co} - 1.4 \times 10^4$.