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OF INTERSTITIALS IN TRANSITION METALS

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Abstract. — This paper resumes the present knowledge about electronic structure and order in carbon-transition metal (Fe, Co, Ni) interstitial alloys. It is shown that the ultra rapid quenching technique (U.R.Q.) allows to obtain extended solid solutions (NiC, CoC, FeC). We define, from X-ray diffraction, Mössbauer spectroscopy and resistivity measurements, the range of the existence of the totally disordered martensitic phase (b.c.c., \( x < 0.003 \)) and of the ordered phase (b.c.t., \( x > 0.04 \)). Resistivity measurements, specific heat, saturation magnetization, N.M.R. and Mössbauer effect allow us to build a model for the electronic structure of carbon in transition metals. This electronic structure is characterized by the existence of two narrow virtual bound states near the Fermi level. The positions of these virtual bound states are adjusted according to our experimental results which display a big difference between strong (Co, Ni) and weak (Fe) ferromagnets. Strong anisotropy of the electronic binding energy of a carbon pair in \( \alpha \)-iron is shown in a preliminary calculation.

In this paper, we summarize some experimental and theoretical results we obtained recently on the electronic structure of interstitials in transition metals (Ni, Co, Fe) with special attention concerning the FeC system. The investigation of the properties of such alloys is quite intricate from the low solubility of interstitials in such metals and also from the large and long ranged interactions between them. A systematic investigation of the electronic structure of such alloys needs: (1) ultra-rapid quenching method (U.R.Q.) to try to extend the solubility limit; (2) a detailed study of the role of the U.R.Q. on the local ordering of interstitials; (3) an experimental study of the electronic properties of interstitials (specific heat, magnetization, transport properties, hyperfine fields, ...); (4) a theoretical study of the electronic structure of isolated interstitials in relation with the previous experimental data, the calculation of the interaction energies between interstitials, the determination of their physical origins (chemical or elastic), their order of magnitude, range and anisotropy.

1. Effects of a ultra-rapid quenching from the melt on some interstitial alloys and on pure cobalt. — The effects of U.R.Q. by using the anvil-piston technique [1] have been investigated in four different cases:

1) In FeC\(_x\) alloys a totally disordered martensitic phase (b.c.c.) can be obtained up to about \( x = 0.04 \). More detailed results are given in § 2.

2) In NiC and CoC, the solid solution limit is extended from 1 at. % to at least 5 at. % [2].

3) In NiB alloys we obtain a precipitation of small particles of defined compounds Ni\(_x\)B or Ni\(_{33}\)B\(_3\); the solid solution limit is extended from 0.1 at. % to 0.5 at. % [3].

4) The hyperquenched pure cobalt displays an ordered arrangement of stacking faults. The following peculiarities are observed:

i) whatever high the quenching rate is, the quantity of retained f.c.c. phase is smaller than 30 %;
ii) the hexagonal phase displays a very large density of stacking faults, the number of which increases with the cooling rate;

iii) these stacking faults are not randomly distributed through the crystal, but occurred periodically. The hyperquenched cobalt can be considered as a superlattice of stacking faults; the unit cell of this structure is still hexagonal with the same «a» and «b» axes as the basic unit cell but the «c» axis «C» is 6 N times as long (3 ≤ N ≤ 13).

2. Investigation of hyperquenched FeC alloys.

2.1 PHASE CHARACTERIZATION OF FeC_{x} ALLOYS FOR 0.01 < x < 0.05. — From previous experimental studies (residual resistivity [2, 3, 5], Mössbauer spectroscopy [4] and X-ray diffraction [4, 6]), we deduced that, for 0.01 < x < 0.04, the FeC_{x} alloys consist essentially of a mixing of disordered (massive) and ordered (tetragonal) martensites; the presence of massive martensite superimposed to the tetragonal phase is attributed to a partial auto-tempering of carbon atoms between the martensitic transformation temperature (Ms) and the room temperature. For x > 0.04, the sample display only the tetragonal martensitic phase. The percentage of retained austenite does not exceed 6 % in volume for x = 0.05.

2.2 APPEARANCE OF THE TETRAGONAL STRUCTURE IN THE LOW CONCENTRATION RANGE (0.002 < x < 0.012) (figure 1). — An extensive investigation of the X-ray diffraction has been carried out in the low concentration limit at 300 K. Let y be the volume fraction of ordered martensite, a_{o}, c_{x} the corresponding lattice parameters, and a'_{c} : the lattice parameter of the disordered martensite. The experimental X-ray line is the superposition of three lines corresponding to three different (hkl) planes, and its intensity for (110) planes can be written as :

\[ I_{\text{total}} = 3(1 - y) I_{a'} + 2y I_{a} + y I_{a'} \]

I is the reference intensity for a family of planes (hkl); this relation assumes that the line profile is the same for the three ones. The experimental results can be summarized as follows :

a) When y = 0 (0 < x < 0.012), the line is symmetric and its position gives the parameter a'_{c} of the disordered phase versus x. The experimental slope of such dependence is da'_{c}/dx = 4 ± 1 x 10^{-3} Å/at. %. This value is slightly small as compared with the value deduced from lattice constants in the tetragonal structure when assuming that all carbon atoms occupy only one sub-lattice :

\[ da'_{c}/dx = \frac{1}{2} \sum_{z} da_{z}/dx \approx 6 x 10^{-3} Å/at. % \]

(calculated with da_{z}/dx = 25 x 10^{-3} Å/at. % and da_{y}/dx = -3 x 10^{-3} Å/at. %).

b) When y ≠ 0, the line becomes asymmetric towards the low angles, due to the very large value of dc/dx (25 x 10^{-3} Å/at. %), and the centre of gravity of the line increases with x much more rapidly than that in the previous case. In order to detect more sensitively the appearance of the tetragonal phase for small y values, the top of the asymmetric line is plotted on the picture instead of its centre of gravity. The picture 1 shows that the tetragonal martensite is present in hyperquenched FeC alloys from 0.3 at. % at 300 K. Thus we can define a lower limit for the concentration dependence of the critical temperature (T_{c}) for the order-disorder transformation in such alloys : dT_{c}/dx > 1000 K/at. %. This value is between Kachaturyan's theoretical estimations [7] calculated with and without correlation effects.

c) The values of y depends essentially on the quenching rate : quicker is the quenching rate, larger is the y value; thus the U.R.Q. technique is sufficient to prevent the decomposition of martensite in Fe_{2}C + ferrite, but is not rapid enough to prevent the diffusion of carbon atom over few interatomic distances which leads to the disordered martensite.
3. Electronic structure of carbon in Ni and α-iron; binding energies between carbon atoms. — Simple models for the electronic structure of interstitial impurities can be determined along the same lines as previously used successfully for substitutional alloys of transition metals [13, 14]: in this case a qualitative comparison between the experimental data (magnetization measurements, electrical resistivity, ...) and the theoretical predictions for the existence of s-d virtual bound states has provided a good understanding of the Pauling Slater curve and of the electronic properties [15]. The same analysis is possible in principle for interstitial impurities but, because of the rather low solubility of interstitials, and the strong interaction between them it is rather difficult to obtain a good systematics.

The experimental data obtained up to now [2, 4, 8, 9] concern: i) the modification of the density of states at the Fermi level deduced from resistivity and specific heat measurements (for NiC and CoC alloys only); ii) the determination of the screening charges \( Z_t \) and \( Z_i \) from magnetization measurements; iii) the local properties (symmetry, extension and importance of the electronic perturbation) on and around the interstitial atom from N.M.R. and Mössbauer experiments.

3.1 Resistivity and specific heat: virtual bound state. — In NiC alloys the large resistivity in the majority spin band \( (\rho_\uparrow) \) [9] and the large electronic specific heat \( [10] \) suggest that a virtual bound state is occurring near the Fermi level. The resistivity \( \rho_\uparrow \) and \( \rho_\downarrow \) associated with carbon in iron and the electronic specific heat have not yet been determined up to now; we know only that in each iron spin sub-band, the carbon resistivities are at least equal to 5 \( \mu \Omega \) cm/at. %.

3.2 Screening charges in «d» band and magnetization measurements. — The magnetization variation per carbon impurity is + 2 \( \mu \) in iron martensitic phase [2], and − 3 \( \mu \) in nickel. The screening charge is then mainly done by the majority spin bands \( (Z_\uparrow = Z, Z_\downarrow = 0) \) in iron, and by the minority spin bands \( (Z_\uparrow = -0.5, Z_\downarrow = 2.5) \) in nickel as suggested by a rigid band model \( (Z_\sigma \) roughly proportional to the density of states at the Fermi level). In transition metals the magnetic moment is mainly carried out by «d» electrons and the large change in magnetic moment shows that the screening is mainly done by «d» bands: a model taking only into account the screening of carbon by «sp» host electrons would not be sufficient.

3.3 Local impurity moment. — In both iron and nickel matrices the hyperfine fields on carbon atoms is small [11, 12]: this suggests that the impurity magnetic moment is small.

3.4 Extension of the magnetic perturbation: anisotropy of the perturbation in b.c.c. FeC. — N.M.R. in CoC [9] and Mössbauer spectroscopy in FeC [4] suggest that the magnetic perturbation extends far from the impurity up to the third shell of metallic neighbours. However, in the f.c.c. matrix, the local symmetry of the o.i.s. is cubic and the magnetic perturbation is isotropic on the atoms of the octahedron. In the b.c.c. matrix the local symmetry of the o.i.s. is anisotropic and the modification of the hyperfine fields \( (\Delta H) \) on the first shell of neighbours reveal this anisotropic character: \( \Delta H = -60 \) kOe for the two iron atoms in dipolar position as compared with \( \Delta H = +15 \) kOe for the four iron atoms in equatorial position with respect to carbon. The anisotropy of this screening originates the tetragonal structure of the ordered martensite.

The electronic structure of interstitials in transition metals can be obtained by a simple extension of the extra orbital (Anderson) model. The interstitial is characterized by its local energy level \( E_i^\sigma \) (\( \sigma \) is the spin) and by the strength of the coupling \( J_\rho = \beta \) between the host and the interstitial orbitals.

The energy levels \( E_i^\sigma \) are determined (for given values of the interstitial exchange integral \( J_\rho \) and \( \beta \)) self-consistently by the Friedel sum rule and by the exchange condition:

\[
E_i^\uparrow - E_i^\downarrow = J_\rho \mu I
\]

\( \mu I \) is the magnetic moment on the carbon site (in Bohr magnetons).

In fact, the extension of the impurity potential on the nearest neighbours of the interstitial must be and has been taken into account self-consistently. This extension is in agreement with Mössbauer data [4].

The electronic structure obtained for NiC [16, 17] and for FeC [18] is then characterized by the existence of narrow virtual bound states sitting near the Fermi level.

Since the work of Zener [19] a great deal of attention has been devoted to the interaction between carbon atoms and to the order-disorder transition of FeC alloys [7]. In all these papers this transition has been attributed to an indirect interaction via the strains induced by the interstitials. Such elastic interactions are long ranged and highly anisotropic; they have been estimated from lattice statics calculation using the experimental values for the dipolar tensor and for the host phonon spectra. However, the elastic interactions are competing with the direct chemical interaction and it is important to be able to compute both of them from the electronic structure. It is fairly easy to calculate the chemical interaction energy between two interstitial impurities from the knowledge of the electronic structure of each isolated interstitial. The preliminary results we have obtained for carbon atoms in α-iron show that the order of magnitude of chemical and elastic interactions could be, in some cases, the same. The chemical interactions are also highly anisotropic. As an example, if we assume that the impurity potential is localized on the interstitial
we found the following results compared with lattice statics calculations (table I):

**Table I**

*Binding energies (in electron volt) of the pairs of C atoms consisting of C atom at octahedral site \( \frac{a}{2} (0, 0, 0) \) (with nearest neighbour iron atom in the \( z \) direction) and C atom at octahedral site \( \frac{a}{2} (x, y, z) \).*

<table>
<thead>
<tr>
<th>( n_0 )</th>
<th>( x, y, z )</th>
<th>Lattice statics (Kurdjumov and Khachatryan [7])</th>
<th>Present calculation</th>
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<td>5</td>
<td>0.2, 0</td>
<td>— 0.075</td>
<td>— 0.191</td>
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</table>

**References**