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ON THE MAGNETISM OF IRON IN CHROMIUM

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Résumé. — Les propriétés magnétiques du fer dans le chrome et les alliages riches en chrome sont interprétées en fonction d’un couplage local avec la modulation de spin de la matrice. Il est suggéré que le comportement de Curie Weiss des atomes de fer isolés dans la phase incommensurable tranverse soit dû à des distorsions progressives de la modulation de spin, induites par le mouvement thermique des moments magnétiques des atomes de fer. Ce mouvement est bloqué dans la phase commensurable. Les paires d’atomes de fer premiers voisins se comportent de façon superparamagnétique dans toutes les phases antiferromagnétiques.

Abstract. — The magnetic properties of iron in chromium and in chromium rich alloys are tentatively interpreted in terms of a local coupling with the spin modulation of the matrix. The Curie Weiss behaviour of isolated iron atoms in the transversal uncommensurate phase is related to possible long range distortions of the spin modulation due to the thermal motion of the iron moments. This motion is frozen in the commensurate phase. Pairs of nearest neighbour iron atoms behave in a superparamagnetic way in all antiferromagnetic phases.

Introduction. — It is known that pure chromium exhibits two low temperature antiferromagnetic phases which, to a good approximation, are sinusoidal modulations of a simple antiferromagnetic structure [1]. The long wave lengths of these modulations are uncommensurate with the lattice parameter and have been related to some structure in the Fermi surface of chromium [2].

The effect of many solute atoms on these structures has been studied, and mostly interpreted in terms of a change in average electron per atom ratio, in a rigid band model.

Some of these impurities such as iron have however, magnetic properties clearly related to a localized magnetic moment. In the case of iron, the simple (commensurate) antiferromagnetic phase also takes over at large concentrations. A detailed study of the magnetic properties of CrFe solid solution [3, 4] and especially the recent measurements on CrFe, Cr(Si, Fe) and Cr(V, Fe) [5, 6], clearly show that the couplings of the iron moments with the spin modulations of the matrix must be taken explicitly into account, and lead to different behaviours in commensurate and in uncommensurate phases. It is the purpose of this paper to discuss in the simplest terms the expected magnetic behaviour and to compare this with experiment.

a) ANTIFERROMAGNETISM OF CHROMIUM. — In pure chromium, the higher temperature antiferromagnetic phase corresponds to a transverse modulation, while the lower temperature phase is a longitudinal one. Both have a wave length \(\lambda_0\) which is large compared with the lattice parameter \(a\), varies continuously with temperature and pressure, and is uncommensurate. This spin modulation is accompanied by a small lattice modulation [7] with a wave length \(\frac{1}{3} \lambda_0\). There are usually equal amounts of domains where the wave vector \(k_0\) lies parallel to the three cube axes.

The possibility that a narrow band paramagnetic metal could exhibit a low temperature antiferromagnetic structure, due to electron-electron interactions, was first pointed out by Slater [8]. Overhauser [9] stressed that a spin modulation with a wave length
near to half the Fermi wave length was especially stable in a free electron metal; and Lomer [2] extended this concept to more realistic Fermi surfaces, pointing out that the spin modulation wave vector should bring the Fermi surface in nearly nesting condition with itself, and that chromium was a likely metal for such an occurrence. This nesting wave vector, which is related to the electronic structure, has a priori no special relation to the lattice parameter; hence it should usually be uncommensurate with it.

If the conditions for the appearance of such a spin modulation can be obtained within second order perturbation, the equilibrium amplitude of the modulation requires a knowledge of higher order terms in perturbation from the paramagnetic metal [10]. As long as the amplitude of the modulation remains small, one can expect the analysis of stability within second order perturbations to give the leading term in the magnetic energy. An energy minimum of order $kBT_N$ per atom ($T_N$ Néel temperature of the modulation) is predicted for a wave vector $k_o$ ($k_o = 2\pi/\lambda_o$) which is near to (but not exactly at) [11] the nesting condition $k_n$. This minimum has a certain width in $k$ space, which is expected to be anisotropic: this width is expected to be smallest in a direction normal to the Fermi surface at the nesting point (Fig. 1). At finite temperatures or in impure metals, the corresponding free energy $F$ minimum is expected to be reduced and broadened, but to preserve the same qualitative features. This pronounced minimum combined with the smallness of the amplitude of modulation apparently leads to domination of one Fourier component of the spin modulation [1, 12], giving a very nearly sinusoidal variation of the spins. However, a higher harmonic lattice modulation is observed by X rays [7] and some theoreticians query the use of second order perturbations in the study of these magnetic structures [13].

The increase in iron concentration $c$ lowers the Néel temperature $T_N$ of the transverse uncommensurate phase TU, and even more the stability of the longitudinal uncommensurate phase LU. At a concentration between 1.5 and 2.3 %, the uncommensurate phases are replaced by a simple commensurate antiferromagnetic structure AF as the temperature is decreased.

The amplitude of the uncommensurate spin modulation increases with iron concentration, while the latent heat of the first order transition to the paramagnetic state increases with increasing iron concentration.

**Fig. 1.** Energy $E$ and free energy $F$ of the spin modulations as a function of its wave vector $k$. $k_o$, equilibrium value of $k$; $k_n$, nesting condition (schematic).

**Fig. 2.** Magnetic phase diagram of quenched CrFe solid solutions. P: paramagnetic; LU: longitudinal uncommensurate; TU: transverse uncommensurate; AF: simple commensurate antiferromagnetic (from [7]).
magnetic state P remains constant [23]. Finally the wave length of the spin modulation increases only slightly with the iron concentration, and the transition between the uncommensurate and commensurate phases is of the first order (Fig. 3).

When one tries to fit these features in a rigid band picture, a number of puzzles appear. It is particularly difficult to explain — why Fe lowers the Néel temperature and keeps the latent heat of the TU ↔ P transition constant, whilst it increases the amplitude of the spin modulation on Cr.

— why the wave length of the modulation increases so little with Fe, before the critical concentration for the AF phase to appear.

c) Magnetism of Iron in Chromium. — The rigid band picture neglects the fact that iron atoms are magnetic impurities. This appears very clearly in the paramagnetic phase, where the iron solute atoms are responsible for a strong Curie Weiss contribution. The magnetic properties of the lower temperature phases have been studied by a number of people [3, 4]. The most recent and detailed measurements in the dilute range [5, 6] refer also to ternary alloys where small additions of silicon or vanadium stabilize respectively the commensurate or uncommensurate phases, without altering significantly the magnetic properties of the iron atoms. These data are recalled in table I.

These results are coherent with the following description:

— Fe atoms being roughly distributed at random, one can usefully distinguish in the low concentration alloys concerned here isolated Fe atoms and nearest neighbour Fe atom pairs

— Atoms pairs always give rise to a Curie Weiss paramagnetism with a very small Curie temperature.

— Isolated atoms give rise, in the high temperature paramagnetic phase, to a Curie Weiss paramagnetism, with a moment of 2 to 2.2 μB per atom. In the low temperature phases, they give rise to a temperature

![Fig. 3. — Variation of the wave vector k₀ of the modulation with iron concentration c and temperature T in the CrFe TU phase. k₀ is in units of 2 π/μ (according to [7]).](image)

<table>
<thead>
<tr>
<th>Alloy</th>
<th>wt % Fe</th>
<th>10⁶ A₀</th>
<th>10¹² B₀</th>
<th>T_N</th>
<th>Fit range</th>
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Table I

Results of fitting χ = (1 - w) (A₀ + B₀ T²) + A + C/(T + T₀) to experimental χ(T) data for CrFe alloys. C_T : Curie constant expected if 2 μB per iron atom
independent paramagnetic contribution which is strong in the LU phase, and decreases in the ratios 4/2/1 when going respectively to the AF and TU phases. In the TU phase, they also give rise to a Curie Weiss paramagnetism.

In table I, the LU and TU phases are observed in Cr 1 Fe, Cr 0.5 V 3 Fe, Cr 1 V 3 Fe; the AF phase is observed in Cr 3 Fe, Cr 2 Si 2 Fe, Cr 2 Si 3 Fe. The alloy Cr 2 Fe is an intermediary case with a more complex behaviour. 

— At helium temperature, only one Mössbauer line seems observed [24-26], indicating perhaps that some iron atoms are still paramagnetic or non magnetic.

d) PROPOSED INTERPRETATION. — Iron being the next nearest neighbour to Cr in the periodic table, and furthermore magnetic, it is expected that its scattering properties dominate the eventual change in band structure it would induce in Cr. This change is anyway out of the rigid band picture.

In the dilute limit, we can therefore assume that the presence of the iron atoms does not change the Cr arrangement at long range. The short range scattering effect should lead to a magnetic coupling between the iron moments and their magnetic surroundings and to a short range perturbation in the magnetic modulation of Cr near to each iron atom.

Because Fe is not very far from Cr in the periodic table, we shall assume the scattering weak. Then the magnetic coupling between Fe and Cr should dominate on the perturbation of the Cr matrix. This is what we shall assume in this very crude discussion.

The role of isolated atoms and of close pairs will be discussed in turn.

1) Isolated iron atoms in the dilute limit. — In the AF phase, each isolated iron atom replaces a chromium atom with a definite up or down magnetic moment. It is thus surrounded by a matrix which aligns its magnetic moment in a definite (up or down) direction. If the isolated iron atoms are distributed at random over the two up and down sublattices, they are expected to be aligned in equal proportions in the two spin directions. Their magnetic configuration should thus be that of an Ising spin glass. Experiments tell us that this freezing persists up to near to the Néel point of the AF structure. This shows that the magnetic coupling of an isolated Fe atom with its surrounding AF matrix is strong, indeed stronger than the AF phase itself. This is not very surprising, as the Fe which replaces a Cr has a larger moment.

Most of the isolated iron atoms are contrarywise not magnetically frozen when dissolved in the incommensurate TU phase.

This would not be surprising for one iron impurity atom in an incommensurate phase :

a) One expects a magnetic coupling with the surrounding matrix with a strength similar to that in the AF phase. Because of this strong coupling, one expects the Fe atom to align its magnetic moment $\mu_F$, parallel to that $\mu_\text{Cr}$ which the Cr atom it replaces would have in pure chromium. This restricts the possible orientations of the iron moments to one direction (up or down) in the LU phase, or to one plane (normal to $k_0$) in the TU phase.

b) To optimize the coupling energy, the modulation is expected to shift its phase so that, in the LU phase, a maximum of amplitude in modulation occurs, with the right sign, on the iron site: the spin modulation is pinned by the impurity, and this pinning will shift the modulation by $\pi$, when the magnetic moment of the iron impurity flips from up to down direction, so as to keep the magnetic coupling with its constant maximum strength. In a similar way, in the TU phase, the spin modulation is shifted so as to bring the magnetic moment of the Cr which the iron atom replaces parallel to $\mu_\text{Fe}$; here, the spin modulation will shift continuously with a rotation of $\mu_\text{Fe}$ normal to $k_0$, again so as to keep the magnetic coupling with its constant maximum strength.

In conclusion, the magnetic moment $\mu_\text{Fe}$ of an isolated iron atom should have a more limited freedom of rotation: from a three-dimensional « Heisenberg » like model in the P phase, one goes to a two-dimensional « XY » like model in the TU phase and to a one-dimensional « Ising » like model in the LU phase. $\mu_\text{Fe}$ keeps free to rotate in the XY plane or to flip up and down along the Ising axis, by shifting the phase of the spin modulation of the matrix which it has pinned down.

Thus in this dilute limit, one expects the isolated iron atoms to contribute a Curie term

$$\chi = \frac{C}{T}$$

with in the P phase $C_3$ isotropic,

- in the TU phase $C_2 \approx \frac{1}{2} C_3$ normal to $k_0$ and 0 parallel to it,

and in the LU phase $C_1 \approx 3 C_3$ parallel to $k_0$ and 0 normal to it.

Thus the average $C_1$ and $C_2$ over the three types of domain equals $C_3$.

The coupling energy of each iron atom with the matrix is independent of concentration and varies little with temperature in this limit except near to $T_N$, where it should vanish. It should thus stabilize the modulated structures, and contribute to an increase in their amplitude and the Néel temperature $T_N$ of the TU structure. Because the iron moments have an entropy decreasing from the P to the TU, then to the LU structure, this should contribute to decrease the Néel temperature of the TU phase and the temperature $T_c$ of LU $\leftrightarrow$ TU phase change with increasing iron concentration $c$. These predictions are qualitatively in agreement with experiment in the TU phase. But the decrease of $T_N$ and $T_c$ with increasing $c$ (Fig. 2)
is too large to be explained merely by a difference in entropy.

Finally, in the uncommensurate phases, there should be a temperature independent susceptibility due to the magnetic iron moments coming out of the magnetic plane (in TU) or axis (in LU) when a magnetic field is applied. This contribution should be roughly in the ratios 2/2/1 when going from the AF to LU and TU phases, provided the stiffness is the same for all these phases. The experimental data show, however, that the LU phase is weaker than the other two phases.

2) Isolated atoms at finite concentration in the TU phase. — If now we have a small but finite concentration of isolated iron atoms, each one will tend to pin down the spin modulation of the matrix in the way that suits its own position and orientation. This will lead to a long range distortion of the spin modulation which will cost energy.

Let us first consider the TU spin modulation. As a rough estimate, we can assume that each isolated iron atom distorts the modulated structure over an equal volume $V$ with a size $\frac{1}{2} \lambda_\parallel$ parallel to $k_0$ and sizes $\frac{1}{2} \lambda_\perp$ perpendicular to $k_0$ (Fig. 4):

$$V \approx \frac{1}{2} \lambda_\parallel \lambda_\perp \approx \frac{a^3}{2} c .$$

![Fig. 4. — Distorted spin modulation around a Fe atom at finite concentrations. The distorted and undistorted surfaces of constant phases are marked respectively by continuous and dashed lines (schematic).](image)

We assume a perfect spin modulation, with wave length $\lambda_0 = 2 \pi/k_0$, at the boundaries of $V$, and the iron moment $\mu_{Fe}$ to rotate normal to $k_0$ by an angle $\theta$ from its equilibrium position of maximum coupling with the undistorted spin modulation. To keep in phase with the rotated iron moment, the spin modulation must be distorted by a compression mode with wave length of the order of $\lambda_\parallel$ and $\lambda_\perp$ in directions parallel and perpendicular to $k_0$, and amplitudes

$$\epsilon_\parallel \approx \frac{\theta \lambda_0}{2 \pi \lambda_\parallel},$$

$$\epsilon_\perp \approx \frac{\theta \lambda_0}{2 \pi \lambda_\perp} .$$

The corresponding distortion energy of the spin modulation can be estimated using a parabolic development of the magnetic energy around the wave vector $k_0$ of perfect modulation (Fig. 1). Per unit volume, the distortion energy can then be written

$$E \approx \frac{1}{2} A_\parallel \delta k_\parallel^2 \epsilon_\parallel^2 + A_\perp \delta k_\perp^2 \epsilon_\perp^2 ,$$

where

$$\delta k_\parallel = 2 \pi/\lambda_\parallel, \quad \delta k_\perp = 2 \pi/\lambda_\perp$$

and $A_\parallel, A_\perp$ are the curvatures of $E(k)$ at $k_0$, measuring the corresponding elastic constants of the spin modulation. Minimizing $E$ with respect to $\lambda_\parallel$ and $\lambda_\perp$ at constant volume $V$, we have

$$\frac{\lambda_\parallel}{\lambda_\perp} = \left( \frac{A_\parallel}{A_\perp} \right)^{1/4} .$$

and

$$E = \frac{3}{2} \frac{A_\parallel}{\lambda_\parallel^2} \frac{\theta^2 \lambda_0^2}{2} = \frac{3}{2} \frac{A_\perp}{\lambda_\perp^2} \frac{\theta^2 \lambda_0^2}{2}$$

$$= \frac{3}{2} A_\parallel^{2/3} A_\perp^{1/3} \left( \frac{c}{4} \right)^{4/3} \frac{\lambda_0^2 \theta^2}{a^4} .$$

We have seen that $A_\parallel \gg A_\perp$. But as a very rough order of magnitude estimate, we can take

$$A_\parallel \approx A_\perp$$

such that

$$E \approx \frac{2 k_B T_N}{a^3}$$

for $\delta k \approx 2 \pi/a$ and $\theta \approx \pi$.

Thus

$$A_\parallel \approx A_\perp \approx \frac{4 a}{3 \pi^2 \lambda_0^2} k_B T_N .$$

And the energy of distortion per isolated iron atom is then

$$E_{Fe}(\theta) = \frac{a^3}{2 c} E \approx k_B T_N \left( \frac{c}{4} \right)^{1/3} \left( \frac{\theta}{2 \pi} \right)^2$$

and the corresponding free energy of distortion should start from this value at low temperatures and tend to zero for $T \rightarrow T_N$, in the same way as the free magnetic energy of the perfect modulated spin structure.

This form of $E_{Fe}$ has a simple physical interpretation : because the uncommensurate spin modulation can freely shift its phase, the energy of distortion
which, for an angle $\theta$, would be of the order of $k_B T N (\theta/2 \pi)^2$ for a distortion limited to one interatomic distance, is reduced by a factor $(4/\pi)^{1/3}$ because this distortion is spread over a distance of the order of

$$\frac{\lambda_1}{a} \approx \frac{\lambda_2}{a} \approx \left(\frac{4}{\pi}\right)^{1/3}$$

there are $(4/c)^{1/3}$ interatomic bonds, each distorted by an angle $(c/4)^{1/3} \theta$, thus with a distortion energy $(c/4)^{1/3} k_B T_0 (\theta/2 \pi)^2$.

Each isolated iron atom should therefore be able to rotate freely with temperature over an angle

$$2 \theta_0 \approx 4 \pi \left(\frac{c}{4}\right)^{1/6} \sqrt{\frac{T}{T_N}}.$$

This angle is larger than $\pi$ for temperatures larger than

$$T_0 = \frac{1}{16} \left(\frac{c}{4}\right)^{1/3} T_N.$$

The coupling of the iron moments with the TU spin modulation should thus introduce a kind of antiferromagnetic behaviour of the iron magnetic moments.

**a)** For $T \geq T_0$, this magnetic coupling with the matrix should lead to a Curie Weiss law of the type

$$\Delta \chi = \frac{C}{T + T_0}$$

where $C$ is the Curie constant for the $XY$ model, and $\Delta T_0$ a negative Curie temperature.

**b)** For $T \approx T_0$, the magnetic coupling with the matrix should lead to a paramagnetic susceptibility which should be nearly temperature independent.

The TU phase is only developed for

$$c \ll 2 \% \text{ Fe}, \quad \text{thus} \quad T_0 < 10^{-2} T_N \approx 3 \text{ K}.$$

For all practical purposes, because of the existence of the LU phase at low temperatures and small concentrations, the condition $T \gg T_0$ applies for the TU phase. One only expects a small antiferromagnetic Curie temperature of a few degrees, in apparent agreement with observations.

The corresponding distortion energy $E_{Fe}$ lowers the stability of the TU phase with respect to the P one as the iron concentration increases. However this is too small to contribute significantly to the observed negative slope $dT_N/dc$. A discussion of the relative stability of the AF versus TU phases should also consider the distortion energy $E_{Fe}$ and entropy of the magnetic iron moments. As $E_{Fe}$ increases with $c$, this increasing rigidity decreases the iron entropy; and this should favour the AF phase at large iron concentrations. A numerical estimate of the critical concentration would require a detailed knowledge of the energy curve of figure 1 and is outside the scope of this paper.

In the dilute range of stability of the TU phase ($c < 2.5 \times 10^{-3}$), the distortion energy $E_{Fe}$ per iron atom is much less than $k_B T_N$ even for large rotations $\theta \approx \pi$. Thus this distortion costs less energy than an uncoupling of the Fe moments from the surrounding spin modulation in the matrix. This is consistent with the picture of each iron atom being free to rotate and pinning down locally the modulation of the matrix to its most favourable phase.

3) **Isolated atoms at finite concentrations in the LU phase.** — A similar analysis can be made for the low temperature LU phase, with similar qualitative conclusions.

In the dilute range of stability of the LU phase, the distortion energy $E_{Fe}$ is less than $kT_N$. One expects the iron moments to pin the phase of the modulation locally so that the modulation presents its maximum amplitude, with the right sign, on the sites of the iron atoms.

At $T > T_0$, the iron impurities should follow a Curie Weiss behaviour $C/(T + T_0)$, where $C$ is now the Curie constant for a one-dimensional (Ising) model and $T_0$ is an antiferromagnetic Curie temperature given by a formula similar to the case of the TU phase. At $T \ll T_0$, the iron moments should be blocked, leading to a temperature independent paramagnetism.

The value of $T_0$ in the LU phase is related to a curvature of $E(\delta k)$ which differs from that involved in estimating $T_0$ in the TU phase. Thus $T_0$ is not necessarily the same in the LU and TU phases. The data of table 1 suggest that, in the alloys studied, $T_0$ is larger than the low temperatures where the LU phase is stable : most of the isolated iron moments are frozen, as in the AF phase.

4) **Close pairs of iron atoms.** — Close iron pairs have much the same behaviour in all the phases concerned, behaving as superparamagnetic pairs of iron atoms with parallel moments, with little or no coupling with the surrounding magnetic matrix, down to He temperature [6]. This might possibly be responsible for some at least of the Mössbauer line of free rotating iron moments reported at low temperatures [24, 26].

As pointed out in [6], the magnetic coupling with the lattice is expected to vanish by symmetry in the AF phase. The two iron atoms of a close pair belong each to one of the interpenetrating simple cubic lattices with opposite spin directions which build up the AF structure of chromium. The centre of gravity of the iron pair is thus a centre of antisymmetry for the magnetic structure of the surrounding chromium matrix. Whatever the orientation of their parallel magnetic moments, each iron atom has a magnetic coupling energy with the matrix which just cancels out that of the other iron atom.

In the LU and TU structures, a cancellation of the same kind can only be approximate, because the wave
length $\lambda_0$ of the modulation is large compared with the lattice parameter $a$ but not infinite.

In the LU structure for instance, with moments modulated along a [100] axis with an amplitude $A_n$ on the $n^{th}$ (100) plane

$$A_n = (-1)^n A_0 \sin \frac{n\pi a}{\lambda_0},$$

it is only the component of the magnetic moment of the iron pair parallel to (100) which is coupled with the surrounding matrix. Within first order perturbations, each iron atom will be magnetically coupled with an energy proportional to the local value that the modulated spin structure would have in pure chromium. The total magnetic coupling energy of the pair is then proportional to the maximum value of

$$|A_n + A_{n-1}| = A_0 \left| \sin \frac{n\pi a}{\lambda_0} - \sin \frac{(n - 1)\pi a}{\lambda_0} \right|$$

$$= 2 A_0 \sin \frac{\pi a}{2\lambda_0} \cos \frac{(2n - 1)\pi a}{2\lambda_0}.$$ 

As $\lambda_0 \gg a$, this is proportional to at most $\frac{\pi a}{\lambda_0} A_0$. For $\lambda_0 > 20a$ (Fig. 3), the reduction factor $\pi a/\lambda_0$ is at most of the order of 0.15 compared with the coupling of an isolated iron with the chromium matrix.

A similar analysis for the TU structure shows that only the transverse component of the magnetic moment of the close iron pair (normal to $k_0$) is coupled with the surrounding matrix. Again the maximum coupling energy is reduced by a factor $\pi a/\lambda_0$ from that for an isolated iron atom.

Thus because $\lambda_0 \gg a$, most of the close pairs should have a rather weak coupling with the surrounding matrix. Because of its large moment, it should thus have a Curie behaviour. In actual fact, the coupling of a close pair with the uncommensurate spin modulation is not at all negligible for a suitable phase shift of the modulation. It is therefore expected that at least at low temperatures the phase of the modulation is pinned by the close pair so as to optimize the magnetic coupling: the situation should be similar to that for isolated atoms, but with a phase condition in quadrature with that for isolated atoms (maximum of the spatial derivative of the amplitude). As for isolated atoms, the distortion of the spin modulation around the pair would lead to only a very small negative Curie temperature for the paramagnetism of the pair, in the range of concentration where close pairs can be distinguished from larger aggregates ($c < 4\%$).

**Conclusion.** — The magnetic behaviour of iron in small concentrations in chromium is consistent with a strong local coupling of the magnetic moment of isolated iron atoms with the spin modulation of the surrounding chromium.

In the antiferromagnetic (commensurate) phase, this coupling freezes out the iron moments of isolated atoms into a Ising type of random spin glass, with only a temperature independent paramagnetism at low temperatures.

In the uncommensurate phases, the moments of the isolated iron atoms should be forced by their coupling with the matrix to take a transverse or longitudinal orientation in the transverse or longitudinal phases respectively. Deviations from these preferred orientations under an applied field lead to a temperature independent paramagnetism. But in the TU phase, the moments should be fairly free to rotate in a plane, forcing the spin modulation to take locally the optimum phase shift for maximum magnetic couplings. This should lead to a Curie Weiss behaviour of the isolated iron atoms, with somewhat reduced Curie constants. In the small concentrations of interest, the ensuing distortions of the spin modulation of the matrix only introduces a negative paramagnetic Curie temperature increasing with the iron concentration and of at most a few degrees. These magnetic distortions of the matrix should make the uncommensurate phases less stable than the commensurate antiferromagnetic one at large iron concentrations. In the LU phase, a more rigid modulated structure apparently freezes out the isolated iron moments in the alloys explored.

Finally, ferromagnetically coupled close iron pairs are expected to behave as superparamagnetic entities, following a Curie Weiss law with a small magnetic coupling of the pair with the AF matrix vanishing by symmetry. In the uncommensurate phases, because the long wave length of the modulation, one expects the maximum magnetic coupling of a pair with the modulation to be smaller than for an isolated iron atom, but of the same order of magnitude. The spin modulation of the matrix might therefore be pinned down and distorted by pairs as it is by isolated atoms; but this will only introduce a negative paramagnetic Curie temperature of negligible amplitude in the range of concentrations where close pairs can be distinguished from larger aggregates.

These conclusions seem in general agreement with experiments. The strong difference of magnetic behaviour of iron in the commensurate and uncommensurate phases seems an interesting consequence of the fact that the phase shift of the spin modulation is blocked in a commensurate phase but free to change in an uncommensurate one.

It would be of interest to explore in more detail, both experimentally and theoretically, the consequences of this model, and especially the low temperature spin wave spectrum of such magnetic solid solutions, both in the commensurate and uncommensurate phases, as well as the reaction to an applied field.
Finally an analysis of the phase diagram seems to require a more detailed knowledge of the effect of iron in chromium, and notably the strength of the magnetic coupling energy of the iron with the surrounding matrix as well as the local distortion of the spin modulation of the matrix, due to the scattering by the iron atoms. In the small concentrations of interest here, it is probable that a treatment at infinite dilution would be sufficient.

Similar behaviour is expected for magnetic impurities dissolved in other modulated antiferromagnetic matrices, especially rare earth metals.

References

[14] FRENKEL, J. and KONTOROVA, T., Phys. Z. Sowjetunion 13 (1938) 1; Fiz Zh. 1 (1939) 137.