

First Measurement of Short-Range-Order Inversion as a Function of Concentration in a Transition Alloy

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Diffuse-neutron-scattering and resistivity measurements have been performed on $\text{Fe}_{1-c}\text{Cr}_c$ alloys ($c < 0.15$). A change of sign of the short-range-order parameters near $c = 0.1$ indicates that the alloys exhibit short-range clustering at $c > 0.1$ and a tendency to form an ordered compound at $c < 0.1$. Concurrently, the slope of the resistivity versus temperature changes its sign. This inversion of short-range ordering has been predicted by a recent calculation. These experiments are considered to be an important confirmation of the theory.

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Attractive or repulsive short-range order (SRO) in $A_{1-c}B_c$ alloys is characterized by the Cowley-Warren SRO parameters,¹ readily determined in a diffuse-neutron-scattering or x-ray experiment. The physical parameters underlying this observation are the interaction pair potentials which may be deduced from the SRO parameters in the mean-field approximation of Clapp and Moss,² allowing a comparison with theoretical calculations. Several theoretical models^{3,4} have been developed in order to relate the interaction pair potentials to the fundamental characteristics of the alloy: They involve finding a suitable expansion of the internal energy so that it may be written as a sum of pairwise interactions. In this context, the transition-metal alloys offer a serious challenge. In these alloys, it was shown that the electronic configurational energy could be written in an expansion of effective pair potentials starting from the completely disordered state (generalized perturbation theory^{5,6,7}) although the cohesive energy cannot.⁸ The model derived for systems in a paramagnetic state reveals the strong variation of the first nearest-neighbor pair potential with the position of the Fermi level in the electronic band and the existence of two critical positions for which the sign of the pair potential changes. This yields a strong variation of the pair potential with concentration, and the possibility of an inversion of short-range ordering in some well-chosen alloys. This possibility has not been experimentally checked, probably because of the difficulties related to the nature of the alloys concerned. In consideration of the very high values of the Curie temperature for metals in the first transition series, the model was thus extended by one of the authors to the ferromagnetic state and applied to Fe alloys.⁹ This modified model predicts that the interaction pair potential between first nearest neighbors in $\text{Fe}_{1-c}\text{Cr}_c$ alloys changes its sign at rather low Cr concentration ($c = 0.25$). This result has

motivated the measurements of SRO parameters by diffuse neutron scattering in $\text{Fe}_{1-c}\text{Cr}_c$ alloys that we report here. As previous experiments¹⁰ had shown that this change of sign did not occur for $c > 0.15$ we have limited our study to three samples of concentration $c = 0.05, 0.1, 0.15$. We show that the alloy exhibits SR clustering for $c > 0.1$ and a tendency towards the formation of ordered compounds for $c < 0.1$. This experimental result gives evidence for a spectacular band effect; moreover, it allows a verification of the theoretical model and hence contributes to the understanding of SRO in transition-metal alloys in a very important way. In as much as theoretical pair potentials are derived for the 0-K ferromagnetic state, it was obviously important to perform measurements on alloys in a stable state of order in the bcc phase, corresponding to an equilibrium temperature as low as possible compared to the Curie temperature. However, very long annealing times at low temperatures are prevented as they could lead to the formation of small quadratic precipitates of the sigma phase. The choice of the appropriate heat treatment required a precise study of the ordering kinetics by resistivity measurements which we describe now.

As previously described,^{11,12} the procedure consists in performing a cycle of isochronal anneals, each anneal being followed by a rapid quench of about 5000 K s^{-1} . The sample resistance is then measured at a reference temperature sufficiently low to enhance the SRO contribution to the resistivity compared to other processes (phonons, magnons). Figure 1 shows the resistance variation as measured at 4.2 K after isochronal anneals of 300 s in temperatures successively decreasing and increasing. This variation can be schematized in two regions. In the high-temperature region, the resistance varies almost linearly with the annealing temperature, which indicates that SRO can be frozen at equilibrium. Very interestingly, in this region, the

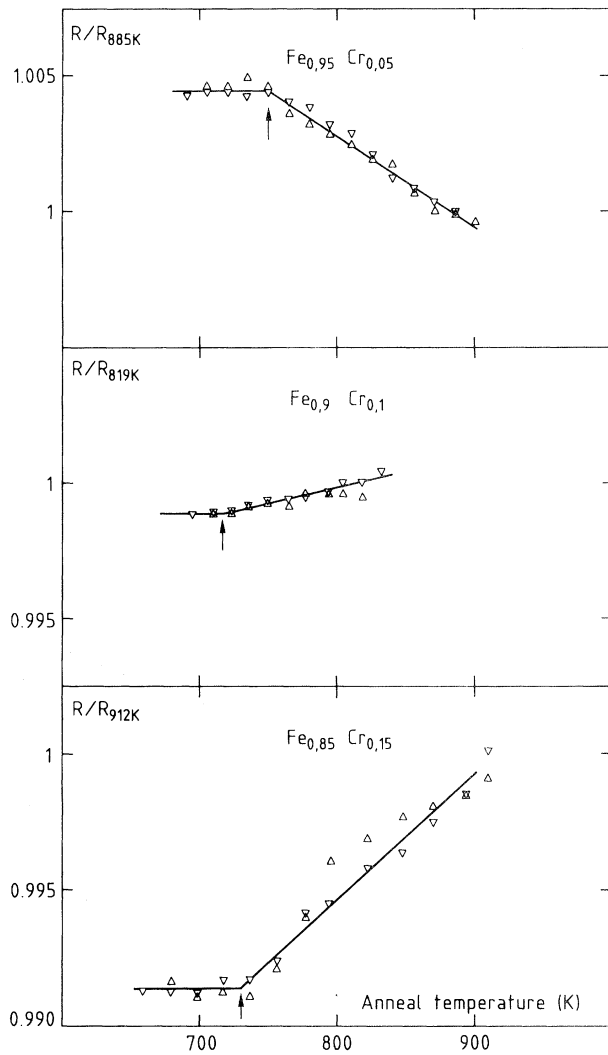


FIG. 1. SRO kinetics of the $Fe_{1-c}Cr$ alloys. Variation of the 4-K resistance referred to its value after a quench from the initial anneal temperature. Triangles and inverted triangles refer, respectively, to up and down cycles.

slope of the resistance versus temperature dR/dT changes its sign when c increases from 5 to 15 at.% Cr. At low temperature, the resistance reaches a plateau showing that, because of the low atomic mobility, a metastable SRO state is obtained. At the temperature corresponding to the knee in the resistance curve, one can roughly consider that the mean ordering time is equal to the annealing time. Following an Arrhenius law for the ordering time, we have thus deduced an average self-diffusion energy for the three concentrations, $E_{sd} = 2.36 \pm 0.1$ eV, in agreement with values deduced from anelastic measurements on $Fe_{0.775}Cr_{0.225}$.¹² By use of this result, adequate heat treatment could be given to

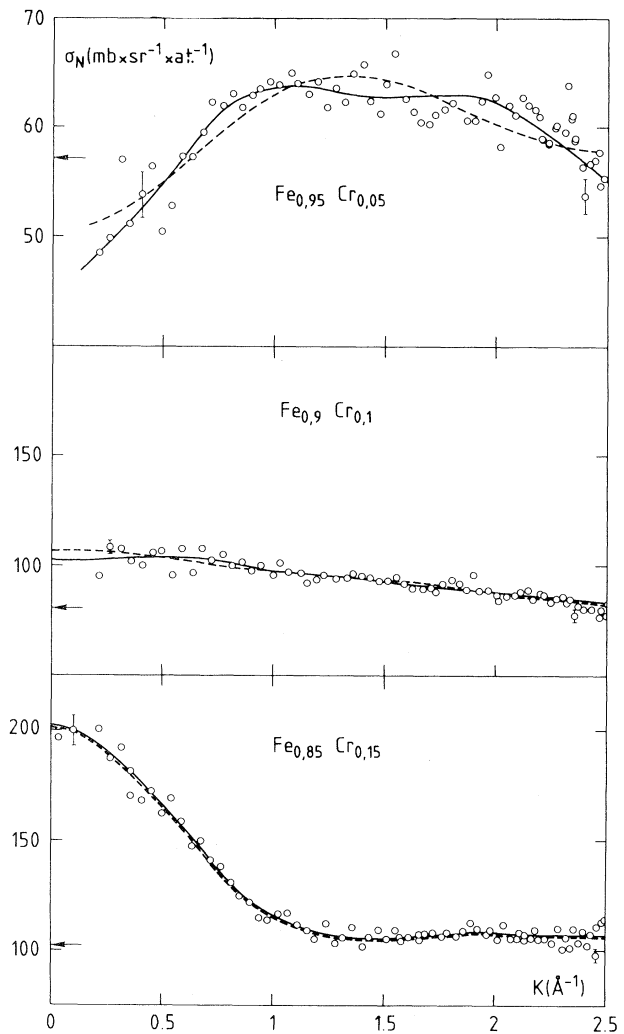


FIG. 2. Nuclear cross section $\sigma_N(K)$ in $mb\ sr^{-1}\ at^{-1}$ as a function of the scattering vector K . The arrows indicate the theoretical Laue plus incoherent cross sections $c(1-c)(b_{Fe} - b_{Cr})^2 + \sigma_{inc}/4\pi$. The lines correspond to fits with three (dashed line) or four (solid line) SRO parameters.

the neutron sample in order to obtain a stable state of order at 703 K. This temperature has to be compared with the Curie temperatures of 1050, 1020, and 980 K, respectively, obtained for 5, 10, and 15 at.% Cr. In the temperature range 793–703 K, the bcc solid solution is generally metastable. Fortunately, the kinetics of the formation of the sigma phase is extremely low compared to the measured ordering kinetics.^{13, 14}

The neutron diffuse scattering of the alloys $Fe_{0.85}Cr_{0.15}$, $Fe_{0.9}Cr_{0.1}$, and $Fe_{0.95}Cr_{0.05}$ was measured in the reactor Orphée (Saclay) with a long wavelength, $\lambda = 4.78$ Å, providing a range of the scattering vector K ($K = 4\pi \sin\theta/\lambda$) of $0.2 < K$

$< 2.5 \text{ \AA}^{-1}$. The elastic nuclear scattering was measured at 77 K and separated from the magnetic scattering by performing two measurements, respectively, with a saturating magnetic field of 15 kOe perpendicular to K and with a zero field. Data have been converted into absolute units by use of a vanadium sample. Figure 2 shows the nuclear cross sections as a function of K . At $c = 0.15$, $\sigma_N(K)$ strongly increases at small K , indicating short-range clustering. This is consistent with previous mea-

surements¹⁰ on an alloy of the same composition quenched from high temperature. At $c = 0.10$, $\sigma_N(K)$ flattens with K and at $c = 0.05$ it is clearly decreasing when K tends to zero. In the FeCr system, where the lattice distortion contribution to the nuclear cross section can be neglected in first approximation,^{10,15} this implies that at small concentrations, short-range order becomes of a repulsive type, i.e., tendency to form ordered compounds. More quantitatively, the nuclear cross sections have been analyzed in the usual way with the equation

$$\sigma_N(K) = \frac{d\sigma_N(K)}{d\Omega} = \frac{\sigma_{\text{inc}}}{4\pi} + c(1-c)(b_{\text{Fe}} - b_{\text{Cr}})^2 \left[1 + \sum_i N_i \alpha_i \frac{\sin(KR_i)}{KR_i} \right]$$

where σ_{inc} is the incoherent cross section of the alloy and b_{Fe} and b_{Cr} are the coherent scattering lengths. N_i , R_i , and α_i are respectively the coordination number, radius, and SRO parameter of the i th neighboring shell.

A least-squares fit of $\sigma_N(K)$ was performed with σ_{inc} and α_i as parameters. σ_{inc} was found close to the usual values but large oscillating values were found for the SRO parameters. Thus we have limited the fit to four α_i 's and expressed our results in terms of the average parameter for the first- and second-neighbor pairs [$\alpha_{1,2} = (8\alpha_1 + 6\alpha_2)/14$], in a procedure usually employed for bcc alloys, where the first- and second-neighbor distances are very close to each other.¹⁶ $\alpha_{1,2}$ can be considered with good confidence, being almost independent of the fitting procedure. At $c = 0.05$ it is close to its maximum negative value [$-c/(1-c)$] and changes its sign near 10 at.% Cr. Pair potentials V_i corresponding to i th neighbor pairs have been derived from the α 's by use of the linearized expression of the Clapp-Moss relationship.² Because of the rather large uncertainties on α_3 and α_4 and thus on V_3 and V_4 , we have limited the comparison with theory to the mean pair potential $V_{1,2}$ between first- and second-neighbor pairs. Moreover from a theoretical point of view, we expect that in transition-metal alloys, first pair potentials play the major role for describing chemical ordering.⁷ The variation of $\alpha_{1,2}$ and $V_{1,2}$ with concentration are shown in Fig. 3. They have been extended to low concentration ($c < 0.05$) on the assumption of maximum repulsion between near-neighbor Cr pairs [$\alpha_{1,2} = -c/(1-c)$]; $V_{1,2} \approx kT/2(1-c)^2$ where $T = 703$ K].

From the above results we notice the obvious correlation between the change of sign of dR/dT and that of the short-range order parameter $\alpha_{1,2}$ versus concentration. The dependence of the sign of dR/dT on that of short-range order parameters,

and especially on α_1 , has been emphasized in several works.^{17,18} Our observations indicate that this dependence must also be valid in the case of ferromagnetic alloys although a true comparison with the model is difficult because of the role of two electronic currents of different spin polarization expected in the ferromagnetic systems.¹⁹ In the inset in Fig. 3, we have compared the variation of

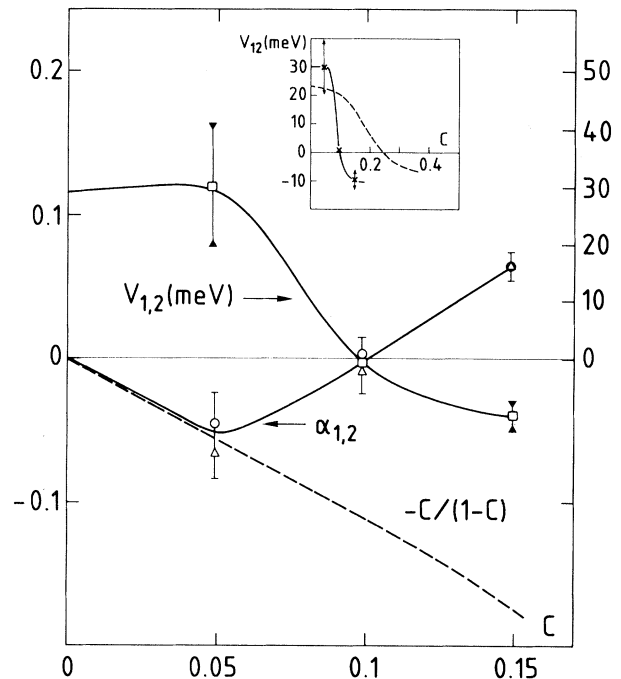


FIG. 3. Variation of the mean SRO parameter $\alpha_{1,2}$ with concentration c ; circles, fit with three α 's; triangles, fit with four α 's; squares, variation of the mean pair potential $V_{1,2}$ in millielectronvolts with c . Inset: variation of $V_{1,2}$ with c : solid line, our experimental work; dashed line, theoretical calculation (Ref. 9).

$V_{1,2}$ as a function of concentration with the theoretical determination deduced from the results of Ref. 9. Although the inversion of the chemical ordering has been predicted to set up at $c = 0.25$ instead of 0.1, the agreement for the amplitude is remarkable. As the Clapp-Moss approximation is only valid at temperatures high compared to the critical temperature T_c for long-range ordering,²⁰ such an agreement may indicate that T_c is very low when $c < 0.15$ as confirmed by a study of the miscibility gap limits.²¹ It is interesting to note that by contrast with FeCr alloys, calculation in $\text{Fe}_{1-c}\text{V}_c$ alloys within the same model yields positive values of V_1 and V_2 in the whole range of vanadium concentration; this result is also in agreement with previous experimental observation.¹⁶

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