Mössbauer study of atomic order in Ni₃Fe. II. The order-disorder transition

J. W. Drijver* and F. van der Woude

Solid State Physics Laboratory, Materials Science Center, University of Groningen, Groningen, The Netherlands

S. Radelaar

Technical Physics Department, Experimental Physics Laboratory, University of Utrecht, Utrecht, The Netherlands

The structural order-disorder reactions in stoichiometric Ni_3Fe were followed "at temperature" using Mössbauer spectroscopy. The transition is of first order. Near the transition temperature T_D the transformation proceeds via nucleation and growth and a two-phase region is observed. In a hysteresis zone below this region the nucleation of the ordered phase is suppressed. This is explained on basis of magnetic interactions. Away from T_D both the ordering and the disordering reactions proceed homogeneously. Upon approach of T to T_D, the kinetics of both reactions slow down.

I. INTRODUCTION

In thermodynamic respect, structural order-disorder transitions do not differ from other phase transitions, and therefore can be divided[1,2] in transitions of first order (classical example Cu_3Au) and of second order (e.g., CuZn). Characteristic features of a first-order transition are: (a) coexistence of old and new phase at the transition temperature; (b) presence of a two-phase region; and (c) nucleation and growth of the new phase near the transition temperature. When the two phases have similar physical properties, these features may be difficult to assess. This sometimes has caused uncertainty about the order of the transition in some order-disorder systems.[3,4]

For Ni_3Fe, which has the $L1_2$ structure like Cu_3Au, a first-order transition is predicted by both Landau's thermodynamic theory[1,2] and atomistic theories as from, e.g., Dienes[5] or Vineyard[6]; this actually has been confirmed by neutron diffraction.[7] Other techniques encounter various difficulties in detecting order-disorder effects, as was already outlined in the preceding paper,[8] hereafter referred to as I. Making use of the microscopic character of the Mössbauer effect (ME) technique, we have been able to observe in Ni_3Fe features (a)–(c) of a first-order transition.[9]

II. EXPERIMENTAL TECHNIQUE

A Mössbauer spectrum of a Ni_3Fe absorber is, below the ferromagnetic Curie temperature T_C (not to be confused with the structural order-disorder transition temperature T_D), composed of a multiple of overlapping six-line patterns. Each pattern corresponds to a magnetic hyperfine field H_{hf}, felt by a ^{57}Fe nucleus at a particular lattice site. Therefore a spectrum shows six asymmetrically broad-

ened lines. In I we determined the long-range-order parameter η in Ni_3Fe from room-temperature spectra. The Ni_3Fe foils employed had been given different amounts of order by annealing at temperatures below 760 K. For such a study a line-profile analysis is necessary from spectra with good statistics, which means long recording times. Obviously, for a kinetic study "at temperature," the recording time must be short with respect to the time, characteristic for the reaction. Fortunately, the average hyperfine field $\bar{H}_{hf}$ and the width of the outer lines Γ already contain valuable information about the order-disorder process, and these parameters are easily obtained by fitting the spectra with six lines. $\bar{H}_{hf}$ is mainly determined by the average atomic configuration around and the average $3d$ moment on the considered Fe atom, and is in these ways related to η. Γ gives information about the distribution of H_{hf} in the sample, which can result both from the statistical variation of atomic configurations and from the coexistence of ordered and disordered phase.

For a correct interpretation of the spectra in the phase-transition region, we first investigated the temperature dependence of $\bar{H}_{hf}$ and Γ for the two Ni_3Fe phases. These results are given in Sec. III. We employed the same equipment and prepared stoichiometric Ni_3Fe foils in the same way as described in I. For the ordered foils at room temperature $\eta \approx 0.88$, disordered foils were obtained by cold rolling. The temperature was kept constant better than ±0.5 K, and the thermocouples were calibrated using the melting points of Zn and Al.

III. TEMPERATURE DEPENDENCE OF THE HYPERFINE PARAMETERS

We determined $\bar{H}_{hf}$ and Γ from 4.2 K up to above T_C for ordered and disordered Ni_3Fe. $\bar{H}_{hf}$ as a
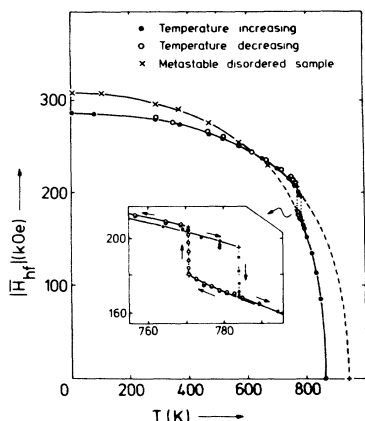
FIG. 1. Average hyperfine field $\bar{H}_{hf}$ vs temperature T at ^{57}Fe nuclei in Ni$_3$Fe. In the inset the transition region is depicted on a larger scale.

function of T is plotted in Fig. 1. The average field of the ordered phase $\bar{H}_{hf,O}$ decreases gradually upon heating, but drops at the transition temperature T_D to the value of the disordered phase. After completion of the reaction the average field of the disordered phase $\bar{H}_{hf,D}$ is measured up to T_C. During cooling the reverse path is followed with a considerable hysteresis. $\bar{H}_{hf,D}$ of a disordered sample could also be measured below 670 K. Further we have indicated in the figure $T_C = 940$ K of the ordered phase, measured by Kollie and Brooks[10] using pulse calorimetry. The inset shows the transition region in more detail. The points on the solid lines correspond to the equilibrium situation; the
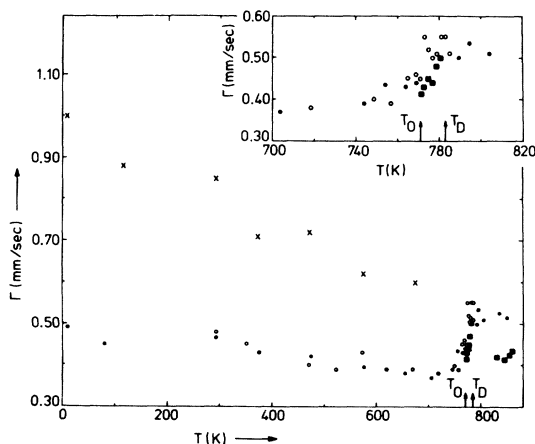

FIG. 2. Temperature dependence of linewidth Γ in ME spectra, taken from ordered ($\bullet$, $\blacksquare$, and $\bigcirc$) and disordered (x) Ni$_3$Fe. $\bullet$ and $\blacksquare$: temperature increasing; $\bigcirc$: temperature decreasing. In the inset the transition region is depicted on a larger scale. Ordering and disordering temperatures (T_O and T_D, respectively), are indicated.

points on the dotted lines were obtained during the reaction.

Γ as a function of T is plotted in Fig. 2. Only data for the equilibrium situation are given. For the interpretation of the spectra it is important to note that near the transition region the line broadening is much smaller than at room temperature, which indicates that in the transition region H_{hf} is only weakly dependent on the surroundings. Apparently, the magnetic moment of an iron atom in an ordered environment experiences a relatively strong exchange field from the surrounding moments, and this effect compensates near T_D the inherently lower hyperfine field at the nucleus of such an atom. The difference between $\bar{H}_{hf,O}$ and $\bar{H}_{hf,D}$ arises mainly from the higher T_C of the ordered phase, and extra line broadening in this region has to be attributed to inhomogeneity in the sample due to the simultaneous presence of the ordered and the disordered phase.

IV. EVOLUTION OF THE ORDER-DISORDER REACTIONS

The order-disorder reactions were followed at constant temperature. We investigated the equilibrium behavior of the alloy by slowly approaching the transition temperature and keeping T constant when the reaction started. Also we studied the reaction following a fast up or down quench.

The ordering reaction was started (after an anneal at 970 K for recrystallization) by cooling from the disordered region with steps of 2 K and two-day anneals (cf. Fig. 1). A first change in the spectra, due to ordering, was observed at 770.9 K; at this temperature the reaction was completed in 200 h. The time evolutions of $\bar{H}_{hf}$ and Γ are shown in Fig. 3(a). Also in this figure the reactions in the same foil, following a quench from 790–757.6 K [Fig. 3(b)] and to 720.2 K [Fig. 3(c)], are shown. The most important difference between Fig. 3(a) on the one hand, and Figs. 3(b) and 3(c) on the other hand is the absence in the latter cases of line broadening during the reaction.

An ordered nonrecrystallized foil was heated through the transition region with steps of 5 K. At 779.3 K $\bar{H}_{hf}$ started to change but attained an equilibrium value (the point on the solid line in Fig. 1) after 11 days. Probably some recrystallization did occur (for all other reactions recrystallized samples were used). At 784.2 K the disordering started and evolved as depicted in Fig. 4(a) with a considerable line broadening during the reaction. This broadening was absent during the reaction at 790.9 K, observed after an upquench from 757.6 K [see Fig. 4(b)].

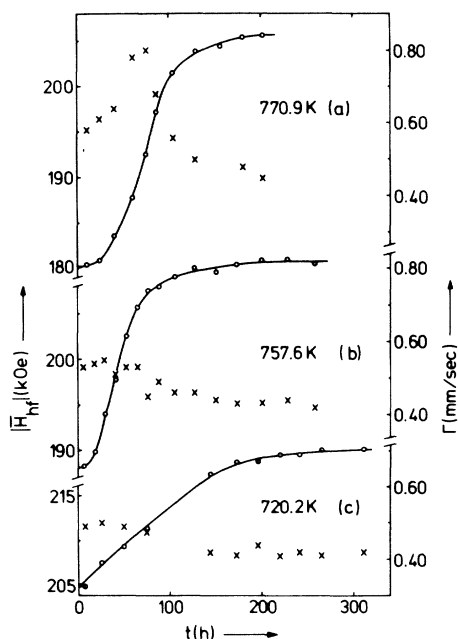For a closer investigation of the gap of 13 K between the highest ordering and the lowest disor-

FIG. 3. $\bar{H}_{hf}$(O) and $\Gamma(x)$ vs annealing time during the ordering reaction at three different temperatures.

dering temperature, we performed a slower dis-ordering run, heating with steps of 1 K and four-day anneals. Between 771 and 780.5 K no abnormal behavior of $\bar{H}_{hf}$ was observed, but Γ increased slightly (see the points ■ in Fig. 2). At 781.8 K the first time-dependent decrease of $\bar{H}_{hf}$ was ob-served, and equilibrium was reached after 250 h [Fig. 5(a)]. After another 250 h the temperature was raised with 1 K, whereupon the hyperfine field started to decrease again [Fig. 5(b)]. When after 600 h the field was still changing, T was further raised with 1 K to 783.8 K. At this temperature the reaction was completed after another 600 h [Fig. 5(c)]. The line broadening during the reaction was considerably larger than expected. These last re-sults can only be understood on basis of the ex-istence of a two-phase region between the ordered-and disordered-phase fields, which will be dis-cussed below.

V. DISCUSSION

A. Order-disorder transformations

Iida[11] distinguished on the basis of extensive ca-lorimetric measurements on Ni₃Fe three steps in the order-disorder process: (a) establishment of short-range-order equilibrium; (b) establishment of long-range-order equilibrium; and, in part si-multaneously with (b), (c) coarsening of antiphase domains. From the discussion at the end of Sec. III it follows that for our measure-
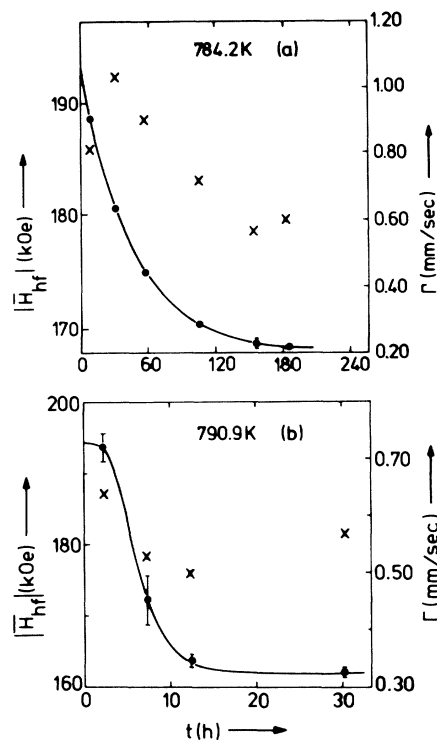

FIG. 4. $\bar{H}_{hf}$ (●) and $\Gamma(x)$ vs annealing time during the disordering reaction at two different temperatures.

ments "at temperature" the change in $\bar{H}_{hf}$ will be substantial only during step (b).

There exists no complete theory for the transi-tion from long-range order to disorder or vice versa.[12] Two approaches can be mentioned for first-order transitions: (i) homogeneous ordering models,[5,6,11] in which the alloy remains homogene-
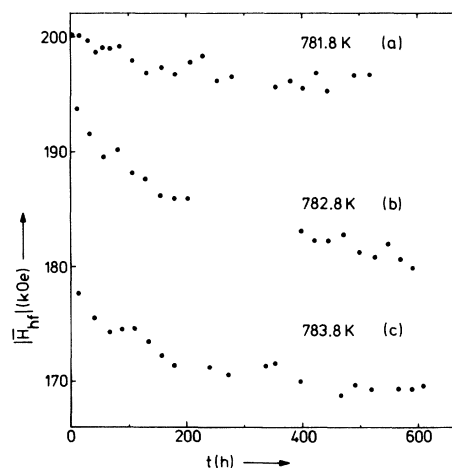

FIG. 5. $\bar{H}_{hf}$ vs annealing time during disordering in the two-phase region. In the course of the reaction the temperature was raised twice with 1 K.
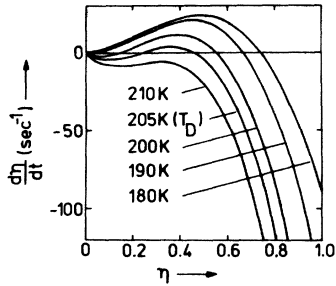
FIG. 6. Reaction rate $d\eta/dt$ as a function of η at various temperatures for an A_3B alloy with transition temperature T_D, according to Vineyard (Ref. 6).

neous in η and this parameter varies continuously during the reaction; and (ii) the nucleation-and-growth model,[13,14] which employs classical nucleation theory. It is important to note that — near the transition temperature T_D — the homogeneous models predict nucleation-and-growth behavior, as is indicated by the virtual parts of the $d\eta/dt$-vs-η curves (cf. Fig. 6, taken from Ref. 6). On the other hand nucleation theory predicts high nucleation rates far away from T_D, leading to a very high density of nucleation centers and thus to a semi-homogeneous transformation. From this point of view the theories are complementary. Also it is interesting that both kinds of theory predict a similar development of the average η as a function of time. In the homogeneous model this results from the behavior of the $d\eta/dt$-vs-η curves, which makes the reaction rate small in the beginning. In the nucleation-and-growth model, the ordering rate is low during the nucleation stage and only becomes appreciable during the growth of the nuclei. Therefore in both models the evolution of the reaction follows a "characteristic" S shape; however, on basis of this shape alone, no choice can be made between a homogeneous or an inhomogeneous reaction.

We mentioned already, that in the ME experiments $\bar{H}_{hf}$ gives information about the average value of η during the reaction. Moreover, extra information is obtained from the behavior of the linewidth, which indicates whether the reaction proceeds homogeneously or not. In order to investigate the line broadening in a more quantitative way, we compared the experimental $\bar{H}_{hf}$ and Γ with the same parameters, obtained from simulated spectra. These consisted of a superposition of two partial spectra of six single lines corresponding to the two phases, where the relative amount was varied with steps of 10%. Field and linewidth values were chosen to be consistent with the data of Figs. 1 and 2. In Fig. 7 we have plotted Γ vs $\bar{H}_{hf}$ for the simulated and the experimental spectra. A
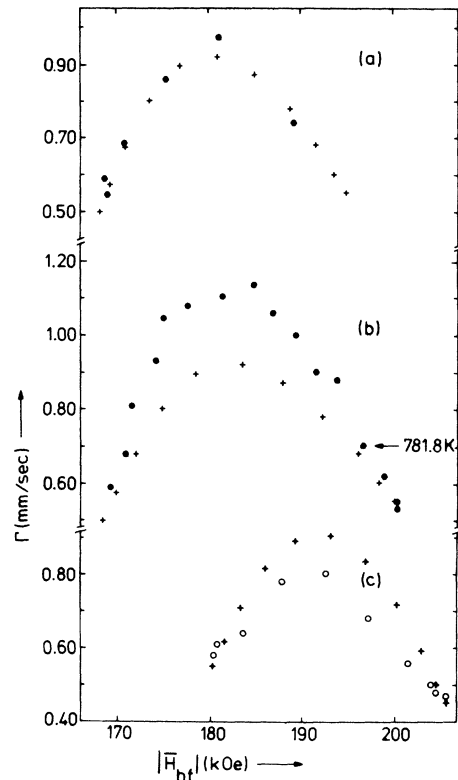

FIG. 7. Linewidth Γ vs average hyperfine field $\bar{H}_{hf}$. (a) Calculated (+) and measured (●) disordering reactions at 784.2 K. (b) Same as (a) but in the two-phase region; the equilibrium point at 781.8 K is indicated. (c) Calculated (+) and measured (○) ordering reactions at 770.9 K.

small correction was performed on the experimental Γ's, in order to account for the change in $\bar{H}_{hf}$ during the collection of a spectrum. The two curves must coincide when the reaction proceeds along the simple nucleation-and-growth mechanism, assumed for the simulated spectra. When however part of the ordering or disordering proceeds as a homogeneous change of order inside the segregates, then the measured curve will lie below the calculated curve.

B. Ordering reaction

Inspection of Fig. 7(c), which depicts the ordering reaction at 770.9 K, shows that the experimental line broadening is somewhat smaller than expected. We attribute this to an initially low hyperfine field inside the precipitates of the new phase. Accordingly we analyzed these spectra as a superposition of two six-line patterns, with $\bar{H}_{hf,D}$ fixed at the initial value, and no constraint on $\bar{H}_{hf,O}$. In Fig. 8, $\bar{H}_{hf}$, $\bar{H}_{hf,O}$, and R (the relative amount of the ordered phase) are plotted. $H_{hf,O}$ extrapolates to
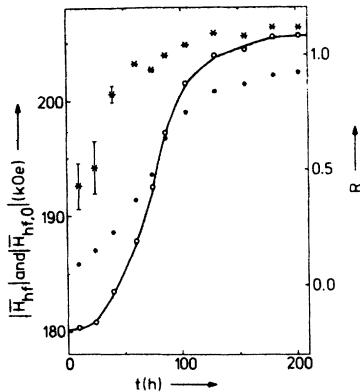
FIG. 8. Time evolution of the average hyperfine field $\bar{H}_{hf}$ (O), of the average hyperfine field of the ordered phase $\bar{H}_{hf,O}$ (*) and of the relative amount of the ordered phase R (●).

about 190 kOe for the first precipitates. This low field can be explained by a low η value. Assuming that $H_{hf} \sim \eta^2$,[15] we estimate that η initially amounts to 0.6 times the equilibrium value. Only more than halfway through the reaction $\bar{H}_{hf,O}$ reaches its equilibrium value.

The low hyperfine field in the first stage of the reaction can also be explained on basis of the absence of line broadening in the spectra near the transition temperature. Only for the spectra from the ordered phase a rise in Γ is observed immediately below the disordering temperature (see the points O and ■ in Fig. 2 for the well-annealed sample between T_O and T_D). Statistical variations in atomic configurations are enhanced near the transition temperature and can serve as nuclei for the new phase. The lack of line broadening indicates that the hyperfine field — and also the local magnetization — in these nuclei is not only determined by the local order but also by the average magnetization in a wider environment. When the precipitates grow, they will pass a critical size, where above the magnetization (the hyperfine field) is only determined by the order inside the precipitates. Clearly this mechanism may contribute to the low value of $\bar{H}_{hf,O}$ in the first stage of the ordering process.

Ordering at the lower temperatures of 757.6 and 720.2 K proceeds homogeneously, as is shown by the complete lack of line broadening [Figs. 3(b) and 3(c)]. The absence of the initial stage at the lowest temperature may be the result of a relatively high vacancy concentration due to quenching. These ordering results are in accordance with the findings in I, where it was shown that the ordering already at 760 K proceeds homogeneously on an atomic scale. A recent field-ion microscopical investigation on Ni₃Fe by Taunt and Ralph[16] appears to con-

firm the homogeneous nature of the reaction at these temperatures. At 753 K no sharp domain boundaries could be observed even at the earliest ordering stages. Instead so-called "order modulations" were detected. Our measurements indicate, that relatively few Fe atoms are near the "zero points" of the order modulations. Coarsening of domains has also recently been studied with x-ray diffraction.[17-19] In Refs. 17 and 18 it was inferred that ordering takes place by nucleation and growth, even below 760 K where we observed a homogeneous reaction. But recently these x-ray results have been attributed to instrumental effects.[19]

C. Disordering reaction

Disordering behaves similarly to ordering as far as the (in)homogeneity of the reaction is concerned. At 790.9 K the disordering proceeds homogeneously [Fig. 4(b)], in accordance with recent results on off-stoichiometric Ni₃Fe.[20] However, at 784.2 K, pure nucleation and growth is observed [Fig. 4(a)], as shown by the similarity of the experimental and simulated $\Gamma - \bar{H}_{hf}$ relations [Fig. 7(a)]. This last reaction starts without apparent nucleation stage. An explanation may be found in electron-microscopical observations,[21] which indicate that disordering starts at the domain boundaries. In this way enough precipitation centers are available to start the reaction.

In the slower disordering run between 781.8–783.8 K a new phenomenon is observed in the linewidth behavior. As shown in Fig. 7(b) Γ is 30% larger than expected. We attribute this to the existence of a two-phase region, which leads to segregation into Fe-rich ordered material with a relatively high $\bar{H}_{hf,O}$ and Fe-poor disordered material with a relatively low $\bar{H}_{hf,D}$. In this way the field difference between the two phases — and thus Γ — is enhanced. Comparison with magnetization data[22] shows that a composition difference of 1-at.% Fe can account for this increase.

D. Phase diagram

The compositional segregation can be understood by considering the phase diagram, which however is not accurately established for the order-disorder transition. Data from the literature[22,23] indicate a maximum transition temperature at 27-at.% Fe, as was confirmed recently.[21] The reason for this shift away from stoichiometry may be found in ferromagnetic interactions: diamagnetic Cu₃Au has its maximum transition temperature at stoichiometry.[3] The difference in ferromagnetic Curie temperatures between ordered and disordered phase is higher in the Fe-rich alloys, and this can cause a stabilization of the ordered phase. In Fig. 9 we
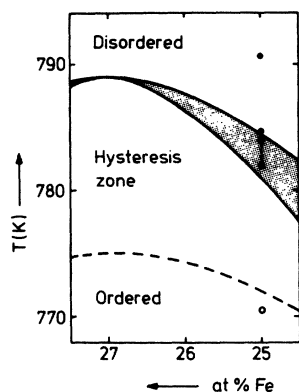
FIG. 9. Tentative phase diagram for the order-disorder transition in Ni_3Fe. The shaded area indicates the two-phase region and the dashed line the temperature where the disorder-to-order reaction starts. Points where ordering (O) and disordering (●) reactions were observed are indicated.

show a tentative phase diagram with a two-phase region (shaded) and a hysteresis zone which also was observed by the authors of Ref. 21. The diagram is adjusted to our stoichiometric data (annealing temperatures which determine phase boundaries are indicated) and is in outline compatible with the data of Refs. 21 and 23. We see that in a stoichiometric alloy disordering can only take place via the two-phase region.

The observed hysteresis is not self-evident. First of all it may be noticed that the hysteresis zone is not symmetric with respect to the two-phase region. Our measurements indicate that the disordering starts immediately when the material is heated to a temperature inside or above the two-phase region. On the other hand the ordering reaction is suppressed and starts only more than 10 deg below the two-phase region. It may be recalled that for the disordering process extended nuclei are available in the form of domain walls, so that the nucleation is inhomogeneous. But nucleation of the ordered phase has to occur by means of clusters of ordered material in the disordered matrix, i.e., by homogeneous nucleation. A relation between hysteresis and this asymmetry of nucleation seems probable.

In the case of homogeneous nucleation, clusters of the new phase are formed continuously. According to nucleation theory[13,14] the nucleation rate of clusters with radius r is strongly dependent on the increase in Gibbs free energy per cluster formed $\Delta G(r)$. Bulk properties give contributions to ΔG, cubic in r. Surface effects give r^2 contributions and oppose nucleation, so that only nuclei surpassing some critical size are viable. Elastic strain energy, arising from a lattice parameter differ-

ence between old and new phase can give a cubic contribution to ΔG and in this way cause hysteresis. This mechanism however cannot explain the observations in Ni_3Fe, because even in Cu_3Au — with a much larger lattice parameter difference — no hysteresis is observed.[3]

However we have already met another mechanism for hysteresis, when we discussed in Sec. V B the rather low value of $\bar{H}_{hf,0}$ during the first stage of the ordering reaction. We supposed that the magnetization of an ordered precipitate initially remains equal to that of the surrounding disordered phase. But any deviation of the magnetization from its bulk value increases the free energy of the precipitate in proportion to its volume, and this leads to an apparent lowering of the ordering temperature. On the other hand, the disordering reaction can evolve inhomogeneously, since nuclei are already present in the form of domain walls. When these nuclei are sufficiently extended, they will have the magnetization of the bulk phase and no hysteresis is expected. In the Appendix we show that such a magnetic contribution can indeed explain our results. We calculated a hysteresis of 13 K which is close to the observed 10 K. An estimate of the hysteresis in Cu_3Au, arising from elastic strain energy, yields the hardly observable value of 1 K.

E. Kinetics as a function of temperature

For a quantitative comparison of the reaction rates we introduce a characteristic time τ, defined as the time, necessary to bring the hyperfine field from its initial value halfway to its final value. As appears from inspection of the Figs. 3 and 4, τ gives information on the initial processes of the reaction, e.g., the nucleation rate.

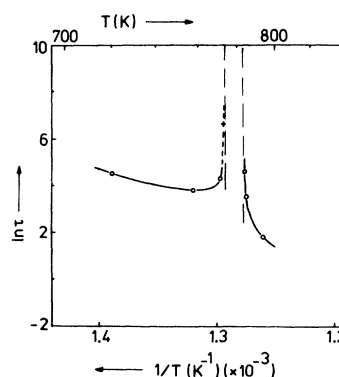In Fig. 10, $\ln\tau$ is plotted versus $1/T$. The half value time at 790.9 K has only limited reliability

FIG. 10. Half-value time τ for the initial stage of the order-disorder reaction as a function of reciprocal temperature.

because of the high disordering rate. The increase of τ near the hysteresis zone is very pronounced. During the two-day anneal at 772.9 K, $\bar{H}_{hf}$ remained constant. The extra point (+) at this temperature is the lowest value for τ, compatible with the experimental error in $\bar{H}_{hf}$. The dashed line through this point is a tentative extrapolation and illustrates the inhibition of nucleation inside the hysteresis zone.

Recently the slowing down of the ordering reaction in Cu_3Au has been interpreted in terms of critical phenomena, characteristic for second-order transitions.[24] In our opinion, such an approach is not justified because of the strong inhomogeneity of the reaction in the transition region.

VI. CONCLUSIONS

Applying the ME technique on the order-disorder transition in Ni_3Fe, we have observed three characteristic features of a first-order transition, viz. coexistence of old and new phase at the transition temperature T_D, nucleation and growth of the new phase for temperatures near T_D, and presence of a two-phase region. Further away from T_D the order-disorder reaction proceeds homogeneously. The hysteresis in the reaction is explained with magnetic interactions, which inhibit the nucleation of the ordered phase. Near T_D a slowing down of the reaction is observed.

ACKNOWLEDGMENTS

APPENDIX

We estimate the increase ΔG_M of the magnetic part of the free energy of an ordered cluster when its magnetization is made equal to that of the surrounding disordered matrix. Then the temperature, below which nucleation of the ordered phase is possible, is shifted from T_D to a lower temperature T_D^*. For small values of $T_D - T_D^*$ it is easily seen that T_D^* is determined by the equation

$$\Delta G_M - (T_D - T_D^*)(S_D - S_0) = 0, \qquad (A1)$$

where S_D and S_0 are the entropies of the disordered phase and of the alloy in equilibrium order just below T_D, respectively. We calculate the necessary parameters in the mean-field approximation, for

a fictitious alloy, with a spin quantum number $s = \frac{1}{2}$ and a ferromagnetic Curie temperature $T_C = 940$ K (the experimental value for ordered Ni_3Fe). This suffices for an order-of-magnitude calculation.

At first the relative magnetization ζ is found from the implicit expression

$$\zeta = \frac{T}{2T_C} \ln \frac{1+\zeta}{1-\zeta},$$

which for $T = T_D = 775$ K yields $\zeta = 0.68$. Experimentally $\zeta = 0.72$ for the ordered phase, with a decrease $\Delta \zeta = -0.16$ upon disordering.[22] Applying the experimental $\Delta \zeta$ to ζ of our fictitious alloy, $\zeta = 0.68$ and $\zeta = 0.52$ are the values for which the magnetic part of the free energy has to be calculated. G_M is given by

$$G_M = -\tfrac{1}{2}kT_C\,\zeta^2 + \tfrac{1}{2}kT\,[(1+\zeta)\,\ln(1+\zeta)$$
$$+ (1-\zeta)\ln(1-\zeta) - 2\,\ln 2\,].$$

Substituting for ζ 0.68 and 0.52 successively, the difference ΔG_M between the values obtained is 3.9 k (erg). $T_D - T_D^*$ follows from relation (A1) when the entropies of both phases are known. The configurational part of the entropy is given by

$$S = -\tfrac{1}{16}k\,[(3\eta+1)\ln(3\eta+1) + 3(\eta+3)\ln(\eta+3)$$
$$+ 3(1-\eta)\ln 3(1-\eta)^2 - 16\,\ln 4\,].$$

Neglecting the difference in magnetic entropy between the two phases, and taking $\eta = 0.8$ as the equilibrium long-range order just below T_D, $S_D - S_0 = 0.21$ k (erg K⁻¹), and (A1) yields

$$T_D - T_D^* = 13\text{ K}.$$

This value is in satisfactory agreement with the experimentally observed hysteresis of about 10 K.

For Cu_3Au we perform a similar calculation, based on strain energy. We assume that small clusters of the ordered phase precipitate coherently with the surrounding disordered phase. Employing the continuum theory of lattice defects for isotropic materials and neglecting the differences in elastic constants between ordered and disordered material, the elastic energy associated with a cluster with volume V and volume misfit ΔV is given by[25]

$$U_{str} = \tfrac{4}{9}\mu(\Delta V)^2/V,$$

where μ is the shear modulus.

For a Poisson's ration $\nu = \frac{1}{3}$, the relation between μ and Young's modulus E is simply given by $\mu = \frac{3}{8}E$. The volume misfit of a unit cell (with four atoms) is $\Delta V = 3a^2\Delta a$, where Δa is the difference

in lattice parameter a between the two phases. We now obtain for the strain energy per atom

$$U_{str,at} = \tfrac{3}{8} Ea(\Delta a)^2 ,$$

which amounts to 0.36 k (erg) when experimental values for a,[26] Δa,[26] and E[27] are substituted. Comparing the value of 0.36 k with $\Delta G_M = 3.9$ k, obtained for Ni_3Fe, a hysteresis of ≈ 1 K is predicted.

*Present address: Technical Physics Department, Experimental Physics Laboratory, University of Utrecht, Utrecht, The Netherlands.

[1]L. D. Landau and E. M. Lifshitz, *Statistical Physics*, 2nd ed. (Pergamon, New York, 1968).

[2]M. A. Krivoglaz and A. Smirnov, *The Theory of Order-Disorder in Alloys* (McDonald, New York, 1964).

[3]F. N. Rhines and J. B. Newkirk, Trans. Am. Soc. Met. 45, 1029 (1953).

[4]L. Guttman, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic, New York, 1956), Vol. 3, p. 146.

[5]G. J. Dienes, Acta Metall. 3, 549 (1955).

[6]G. H. Vineyard, Phys. Rev. 102, 981 (1956).

[7]V. I. Goman'kov, I. M. Puzei, and A. A. Loshmanov, Kristallografiya 10, 416 (1965) [Sov. Phys.-Crystallogr. 10, 338 (1965)].

[8]J. W. Drijver, F. van der Woude, and S. Radelaar, preceding paper, Phys. Rev. B 16, 985 (1977).

[9]A preliminary report has been given in Phys. Rev. Lett. 34, 1026 (1975).

[10]T. G. Kollie and C. R. Brooks, Phys. Status Solidi A 19, 545 (1973).

[11]S. Iida, J. Phys. Soc. Jpn. 9, 769 (1955).

[12]H. Yamauchi and D. de Fontaine, in *International Symposium on Order-Disorder Transformations in Alloys*, edited by M. Warlimont (Deutsche Gesellschaft für Metallkunde, Tübingen, 1973), p. 148.

[13]D. Turnbull, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic, New York, 1956),

Vol. 3, p. 225.

[14]J. W. Christian, *The Theory of Transformations in Metals and Alloys*, 2nd ed. (Pergamon, New York, 1975).

[15]J. W. Drijver, Ph.D. thesis (University of Groningen, 1975) (unpublished).

[16]R. J. Taunt and B. Ralph, Phys. Status Solidi A 24, 207 (1974).

[17]Y. Calvayrac and M. Fayard, Phys. Status Solidi A 17, 407 (1973).

[18]D. G. Morris, G. T. Brown, R. C. Piller, and R. E. Smallman, Acta Metall. 24, 21 (1976).

[19]F. Bley and M. Fayard, Acta Metall. 24, 575 (1976).

[20]G. T. Brown, D. G. Morris, and R. E. Smallman, Philos. Mag. 34, 491 (1976).

[21]Y. Calvayrac and M. Fayard, Mater. Res. Bull 7, 891 (1972).

[22]R. J. Wakelin and E. L. Yates, Proc. Phys. Soc. Lond. B 66, 221 (1953).

[23]E. Josso, J. Phys. Radium 12, 399 (1951).

[24]T. Hashimoto, T. Miyoshi, and H. Ohtsuka, Phys. Rev. B 13, 1119 (1976).

[25]J. D. Eshelby, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic, New York, 1956), Vol. 3, p. 79.

[26]D. T. Keating and B. E. Warren, J. Appl. Phys. 22, 286 (1951).

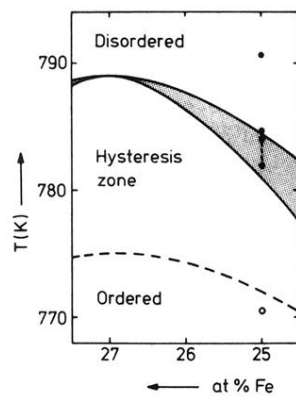[27]L. R. Weisberg and S. L. Quimby, J. Phys. Chem. Solids 24, 1251 (1963).

FIG. 9. Tentative phase diagram for the order-disor-
der transition in Ni$_3$Fe. The shaded area indicates the
two-phase region and the dashed line the temperature
where the disorder-to-order reaction starts. Points
where ordering (○) and disordering (●) reactions were
observed are indicated.