PHYSICAL REVIEW B VOLUME 62, NUMBER 2 1 JULY 2000-II

Fe_3Ni-type chemical order in $Fe_{65}Ni_{35}$ films grown by evaporation: Implications regarding the Invar problem

K. Lagarec and D. G. Rancourt*
Department of Physics, University of Ottawa, Ottawa, Ontario, Canada K1N 6N5

(Received 18 November 1999; revised manuscript received 31 January 2000)

By use of Monte Carlo simulations of chemical ordering, magnetic ordering, and magnetovolume thermal effects and by reviewing the known effects of chemical order in the face-centered-cubic Fe-Ni alloy system, we show that the observations of Dumpich *et al.* [Phys. Rev. B **46**, 9258 (1992)], who report unique Invar-composition $Fe_{65}Ni_{35}$ samples that exhibit Invar behavior despite being collinear ferromagnets with no deviation from the Slater-Pauling curve, are consistent with the effects of varying degrees of Fe_3Ni-type chemical order, which in turn are consistent with the sample preparation and treatment methods used. This allows us to make certain conclusive statements concerning models for Invar behavior and the nature of Fe_3Ni.

I. INTRODUCTION

Guillaume was awarded the Nobel prize in physics in 1920 for his 1897 discovery of Invar, face-centered-cubic (fcc) $Fe_{65}Ni_{35}$.[1] Since that time, the Invar problem has consisted in finding the correct microscopic mechanism for the Invar effect, a near-zero thermal-expansion coefficient that persists in a broad temperature range near room temperature (RT). Early models, such as Guillaume's proposal that the proximity of the martensitic transition (at ~70 at. % Fe, RT) must play a key role, were abandoned for models that all acknowledge the essential role of some aspect of Invar's magnetism but that are very different from one another. These have included: the two-γ-state model of Weiss,[2] the weak itinerant ferromagnetism model of Wohlfarth,[3] and a local moment model known as latent antiferromagnetism.[4] A high degree of sustained interest in the problem is evident from international conferences and symposia, several review articles,[5] and several commemorative articles written for the occasion of the 100th anniversary of Invar's discovery.[6]

The two main competing current views are: (i) two-γ-state-like models in which the Invar effect is ascribed to thermal excitation of a low moment state or to thermal stabilization of the low moment phase, as temperature is increased,[7] and (ii) the latent-antiferromagnetism-like local moment frustration model of Rancourt and Dang,[8] in which Invar behavior occurs due to the combined effect of frustrated exchange bonds and a large and positive magnetovolume coupling parameter, in a predominantly high moment alloy having moment magnitudes that are not sensitive to changes in temperature at the temperatures of interest. These two positions represent two fundamentally different mechanisms, each of which is proposed to be the main cause of Invar behavior, although both may be occurring simultaneously to some extent. The first type of model requires modification in order to explain the undeniable observation that Invar behavior is directly mediated by the alloy's ferromagnetism and disappears at the Curie point on increasing the temperature, whereas this observation is a natural consequence of the local moment frustration model.

One approach in attempting to discriminate these two models is to note that the first does not seem to require exchange bond frustration or noncollinear spin structures whereas the second model seems to require both of these features. In this context, the recent measurements of Dumpich *et al.*[9] are particularly relevant because $Fe_{65}Ni_{35}$ samples are described that have Invar behavior despite being collinear ferromagnets without any deviation from the Slater-Pauling curve. The Slater-Pauling curve in Fe-Ni is a straight-line relationship between the average saturation magnetic moment per atom and composition that extends from $2.8\mu_B$/atom for Fe to $0.6\mu_B$/atom for Ni and that implies stable Fe and Ni moment magnitudes and moment collinearity, in agreement with other measurements where it is found to hold.[10,11] One is tempted to conclude both that moment noncollinearity is not required for Invar behavior in $Fe_{65}Ni_{35}$ and that any model that requires exchange bond frustration must be incorrect.

Before one draws such conclusions, however, it would be important to understand how the unique samples of Dumpich *et al.* can have such properties that had not previously been reported in Fe-Ni alloys, where Invar behavior has always been observed to be accompanied by moment noncollinearity and deviation from the Slater-Pauling curve. The relevant questions are: What physical mechanism gives these unique samples their unusual behaviors and how did these samples acquire the physical or chemical characteristics that lead to these behaviors? Dumpich *et al.* proposed a tentative explanation in terms of an ill-defined ''absence of premartensitic effects.'' In the present paper we argue that the latter explanation is unlikely and we show that all of the observations of Dumpich *et al.* can be explained in terms of varying degrees of chemical order, which in turn are consistent with the sample preparation and treatment methods used. We are then able to make some conclusive statements regarding proposed models for Invar behavior.

We first review the results of Dumpich *et al.* before systematically describing how chemical order would affect each of the observed properties and why we expect Fe_3Ni-type chemical order to have occurred. We use Monte Carlo (MC) simulations of chemical ordering, magnetic ordering, and magnetovolume thermal effects to provide quantitative esti-

TABLE I. Comparison of the properties of the as-prepared and annealed films as measured by Dumpich *et al.* (Ref. 9).

Property	As-prepared film	Annealed film
Average linear thermal expansion coefficient between 100 and 350 K (α)	$\approx -2\times10^{-6}$ K^{-1}	$\approx 1\times10^{-6}$ K^{-1}
Lattice parameter (a)	3.589 ± 0.005 Å	3.606 ± 0.005 Å
Saturation magnetization ($\mu_0/\mu_{Slater\text{-}Pauling}$)	1.0	0.84
Curie temperature (T_C)	700 K	520 K
Hyperfine field distribution [$P(B)$] (Ref. 13)		
most probable value (B_P)	31.5 T	30 T
average value (B_{avg})	31.5 T	27 T

mates wherever possible and make comparisons between the disordered alloys and the known FeNi and $FeNi_3$ ordered structures.

II. STUDY OF $Fe_{65}Ni_{35}$ FILMS BY DUMPICH *et al.*

In a series of articles, Dumpich *et al.* presented the results of structural and magnetic measurements performed on thick ultrahigh vacuum evaporated Fe-Ni films grown at RT.[9,12–14] In most cases, because the film compositions were close to the martensitic transition boundary, both face-centered-cubic (fcc) and body-centered cubic (bcc) phases were produced in each film, making an independent analysis of the fcc phase's properties complicated when not impossible. After refining their growth method, they succeeded in producing a 200-nm-thick film with a pure fcc phase at the Invar composition of 65 at. % Fe by growing it on top of a 50 at. % Fe fcc film, thereby stabilizing the fcc phase.[9] We concentrate on the films reported in the latter article, since we can clearly associate their behaviors and properties to those of the bulk fcc $Fe_{65}Ni_{35}$ alloy.

Dumpich *et al.* measured the magnetization and the lattice parameter as a function of temperature of an as-prepared film, as well as of the same film, after it had been annealed at 900 K. We follow Dumpich *et al.* in naming the film produced at RT the ''as-prepared'' film and the one obtained after annealing the ''annealed'' film. Although measurements of the annealed film were consistent with measurements of bulk $Fe_{65}Ni_{35}$ Invar, the as-prepared film showed significant differences. In particular, contrary to bulk $Fe_{65}Ni_{35}$, its saturation magnetization was consistent with the Slater-Pauling relation, indicating it was a high moment collinear ferromagnet. Inspection of its lattice parameter between 100 and 350 K revealed it also had a low thermal-expansion coefficient, as is found in bulk $Fe_{65}Ni_{35}$.

These results are of critical importance regarding the Invar problem. They suggest that deviation from the Slater-Pauling relation is not required for the Invar effect to occur. This implies that all the theories which rely on a disordered magnetic moment configuration to explain the Invar effect in Fe-Ni alloys must be wrong. The model of latent antiferromagnetism[4] that takes the deviation from the Slater-Pauling curve as its basis is thus, at best, incomplete and the proposed interpretation of the most recent electronic structure calculations of van Schlifgaarde, Abrikosov, and Johansson[15] must be flawed. In the latter calculations, the authors allowed for spin orientation disorder as well as spin magnitude variation to find the ground-state energy curve as a function of lattice volume. They argued that the disordered spin structure is necessary to produce the correct energy curve which produces a zero thermal-expansion coefficient (the Invar effect) at $T=0$ K. The measurements of Dumpich *et al.* clearly show that a collinear spin structure can also produce the Invar effect in $Fe_{65}Ni_{35}$. Only a model (or interpretation) which is consistent with these observations, as well as the large amount of existing experimental data, can be correct. Such a model should also explain how spin collinearity can occur in some samples but does not occur in bulk quenched samples of the same composition.

In addition to the saturation magnetization and the presence of an Invar effect, a few additional properties of the as-prepared and annealed films are worth noting. The lattice parameter of the as-prepared film is slightly smaller than that of the annealed film. The Curie temperature of the as-prepared film is substantially higher than that of the annealed film. Finally, even though ^{57}Fe Mössbauer measurements were not performed on the films from their latest study, Dumpich *et al.* had previously measured the Mössbauer spectrum of a similar film which contained both fcc and bcc phases.[12,13] The extracted hyperfine field distribution of the fcc phase was much narrower than that of bulk $Fe_{65}Ni_{35}$, and did not show a large probability density at low hyperfine field values. A compilation of the observed properties of the two films is given in Table I.

In an effort to explain these unusual results, Dumpich *et al.* proposed that deviations from the Slater-Pauling curve and the broad hyperfine field distribution were due to spin canting arising from ill-defined ''premartensitic effects,'' which were argued to be absent in the as-prepared film. Since these results have been published, several electronic structure calculations on Fe-Ni alloys have shown that spin canting and/or antiparallel alignment occurs primarily because of local Fe-rich environments, not because of lattice distortions or strain effects.[15–17] The difference between the two films is thus most likely due to differences in populations of local environments having different Fe concentrations, which we show are a consequence of chemical ordering that occurs in the as-prepared film and that is removed by annealing in the annealed film. In the following sections, we show both why chemical ordering of the Fe_3Ni type is expected to occur and, by modeling using MC methods, how chemical ordering can explain all of the above-mentioned properties of the two films.

III. MONTE CARLO SIMULATIONS OF CHEMICAL ORDER, MAGNETIC PROPERTIES, AND THE INVAR EFFECT IN Fe-Ni ALLOYS

In order to show why and how chemical ordering can explain the differences between the as-prepared and annealed films, we have performed three different MC simulations. In the first, we include combined magnetic and chemical interactions to determine what type of chemical order is expected at RT, which is the synthesis temperature of the as-prepared film. In the second, standard magnetic only simulation is performed to evaluate the differences in magnetic behavior between a lattice that is chemically disordered, as found in the annealed film, and one which contains a certain degree of order, as is postulated for the as-prepared film. Finally, we perform isothermal-isobaric MC simulations[18] that allow freedom of both individual atomic positions and magnetic moment directions and that use: a Lennard-Jones potential to describe nearest-neighbor (NN) chemical interactions, an Ising model for magnetic NN interactions, and the usual magnetovolume coupling in terms of an interatomic distance dependence of the exchange parameter. The latter simulation includes the possibility of magnetic frustration and allows one to show how the Invar effect arises from Fe-Fe magnetic bond frustration in both the disordered alloy and the chemically ordered alloy (i.e., in both the as-prepared and annealed films), in accordance with the local moment frustration model of Rancourt and Dang.[8]

A. Chemical ordering in Fe-Ni alloys

Above 1200 K, all alloys in the Fe-Ni binary system occur as solid solutions in the chemically disordered fcc (γ) phase. At RT, one finds that $FeNi_3$ and FeNi can form chemically ordered structures, but they are rarely observed in quenched samples because atomic diffusion in Fe-Ni alloys is too slow at the ordering temperatures of interest. $FeNi_3$, which has a chemical ordering temperature of 790 K,[19] can be synthesized by heat treatment but FeNi, which has been discovered in meteorites that cooled with exceedingly small rates,[20] can only be synthesized by particle irradiation because its ordering temperature is 594 K.[21] Based on thermodynamic calculations, Fe_3Ni should also be structurally more stable than its disordered counterpart, γ-$Fe_{75}Ni_{25}$.[22] In addition, Fe_3Ni-type ordering is predicted to occur at compositions between 62 and 77 at. % Fe at temperatures below 470 K.[22] This type of ordering has not, however, been observed experimentally for two reasons: (i) at RT, alloys with more than 70 at. % Fe transform via the martensitic transition to the bcc phase and (ii) below 500 K, the diffusion of Ni in the solid is too slow to allow ordering in reasonable times.[23] Also, it is not found in meteorites because at higher temperatures than the top of its stability field, a spinodal decomposition presumably occurs that produces an Fe-rich and an Fe-poor phase. An example of this is the Santa Catharina meteorite, which is nearly pure fcc Fe-Ni, with a bulk composition of 65 at. % Fe, but which has separated into tetrataenite (chemically ordered FeNi) and a low-moment $Fe_{86}Ni_{14}$ phase.[24]

Dumpich *et al.* grew the as-prepared film at RT, well below the predicted ordering temperature of 470 K. In addition, since they used an evaporation method the atoms forming the film are deposited on the surface with some residual kinetic energy. According to surface diffusion measurements on fcc Ni,[25] the surface diffusion coefficient is approximately an order of magnitude larger than in the solid, which would enable the atoms to establish at least local chemical order as the film grows. Because the film was grown on an underlying substrate of $Fe_{50}Ni_{50}$, long-range chemical order will not necessarily occur but chemical ordering at the NN or next-NN level can be expected. Since the magnetic properties of Fe-Ni alloys are expected to be primarily due to NN interactions, they are, in turn, expected to be sensitive to local chemical ordering effects.

In order to characterize chemical order in Fe-Ni alloys and study its effect on magnetism, Dang and Rancourt[26] introduced a MC algorithm to model chemical ordering by using NN chemical pair energies as well as an Ising model for magnetism with NN interactions. The Hamiltonian is

$$H=-\sum_{\langle nn\rangle} U_{ij}-\sum_{\langle nn\rangle} J_{ij}\frac{\mu_i\mu_j}{4\mu_B^2}, \tag{1}$$

where we have used $U_{\mathrm{NiNi}}=8590$ K, $U_{\mathrm{FeNi}}=9200$ K, and $U_{\mathrm{FeFe}}=8400$ K. These values, which are those reported in Ref. 26 give the correct cohesive energy for pure Ni, and reproduce the correct ordering temperatures for $FeNi_3$ and FeNi. The magnetic exchange parameters used are $J_{\mathrm{NiNi}}=700$ K, $J_{\mathrm{FeNi}}=355$ K, and $J_{\mathrm{FeFe}}=-20$ K, and $\mu_{\mathrm{Ni}}=0.6\mu_B$ and $\mu_{\mathrm{Fe}}=2.8\mu_B$ are the moments which correspond to the Slater-Pauling relation. These parameters reproduce the correct magnetic ordering temperature (Curie temperature) and saturation magnetization for Fe-Ni alloys for concentrations up to 60 at. % Fe.[27] Limits of application of local moment models such as the one expressed in Eq. (1), due to local moment magnitude variations with local chemical environment, have been discussed.[28]

We first ran a simulation for a 4000 atom cell with 65 at. % Fe, periodic boundary conditions, and at the temperature of 300 K, to determine the state of the chemical order that is expected to occur in the as-prepared film. A specific equilibrium configuration was saved and used in the MC simulations described below. We refer to the latter configuration as the ''ordered configuration.'' In addition, a randomly generated chemically disordered configuration is referred to as the ''disordered configuration.''

Since U_{FeNi} is larger than U_{NiNi} or U_{FeFe}, Fe-Ni bonding is preferred, as is evident in the known structures of FeNi and $FeNi_3$. The most notable effect of chemical order should therefore be well characterized by the distribution of atoms around a central Fe atom. In particular, Fig. 1 shows the probability of having a certain number of Fe NN's around an Fe atom in the disordered and ordered configurations. The disordered configuration leads to a binomial distribution with an average of 7.8 NN Fe atoms (0.65×12 NN), whereas the ordered configuration is characterized by a sharper peak with an average of 6.8 NN Fe atoms. A very important difference whose implications are discussed in the next section is that there are no Fe atoms in the ordered configuration with nine or more Fe NN's, as opposed to the disordered configuration, where 35% of the Fe atoms have nine or more Fe NN's. To

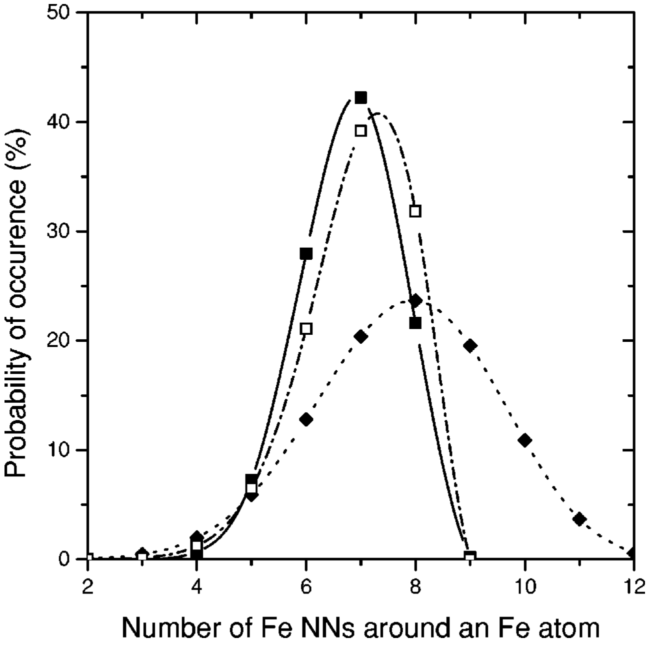

FIG. 1. Probability distributions of finding a certain number of Fe NN atoms around an Fe atom for various configurations: (filled squares) the ordered configuration described in the text, (filled diamonds) the disordered configuration, and (open squares) an Fe_3Ni lattice where 13% of the Fe atoms have been randomly substituted by Ni atoms.

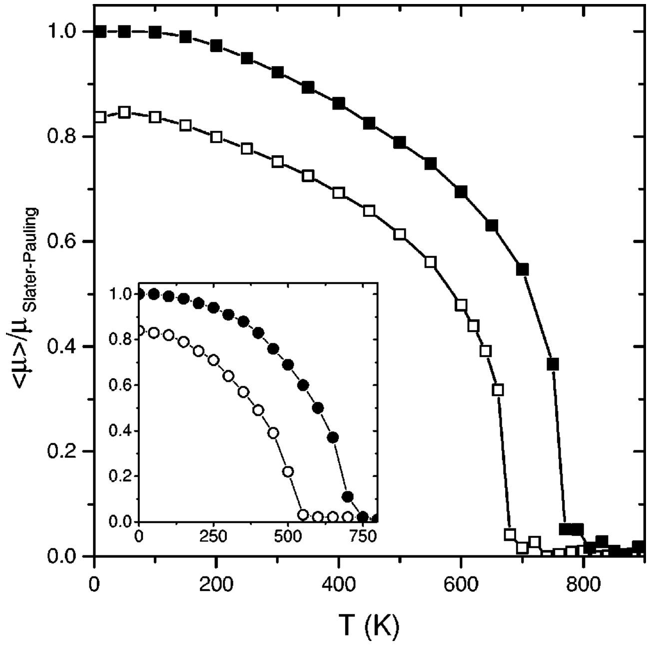

FIG. 2. Average magnetic moment relative to the saturation magnetic moment derived from the Slater-Pauling curve: (filled squares) ordered configuration, (open squares) disordered configuration. Inset: The measured magnetizations of the as-prepared (open circles) and annealed (filled circles) films (Ref. 9).

show that the chemical ordering is of the Fe_3Ni type, we also show a distribution corresponding to Fe_3Ni, where 13% of the Fe atoms have been randomly substituted by Ni to obtain a bulk composition of 65 at. % Fe (Fig. 1). The similarity of this distribution with that of the ordered configuration is striking and shows that in the ordered configuration Fe_3Ni-type ordering is dominant. The slight difference between this latter distribution and the distribution from the ordered configuration suggests that the 13% of Fe atoms which are substituted must not simply be randomly substituted, but must also be arranged to maximize the number of Fe-Ni bonds. Other tests, such as investigating long range order parameters, have also shown the ordering to be of the Fe_3Ni type, rather than of the Fe-Ni type.

B. Magnetic properties of chemically ordered and disordered $Fe_{65}Ni_{35}$ alloys

After synthesis, the films produced by Dumpich *et al.* should behave like bulk materials, with small diffusion rates at usual temperatures. Because of the slow diffusion, any measurement made below or above the synthesis temperature will not significantly affect the chemical order unless it is performed at sufficiently high temperature and for a sufficiently long time. Their annealing process has transformed the as-prepared film into a disordered bulklike material presumably because the annealing time was long enough. Magnetic measurements made on the sample do not require much time, so we expect the measurements to be characteristic of the chemical order at the time of the synthesis, as is the case with FeNi[29] and $FeNi_3$.[19,30] In order to simulate the magnetic properties, we therefore used a specific chemical configuration and allowed freedom of the magnetic moments only. In such a case, the Hamiltonian is reduced to a standard Ising Hamiltonian with NN interactions:

$$H=-\sum_{\langle nn\rangle} J_{ij}\frac{\mu_i\mu_j}{4\mu_B^2}, \tag{2}$$

where the parameters are the same as in the previous section. A standard metropolis algorithm is used to obtain thermal averages of the magnetization. Figure 2 illustrates the resulting ratio between the average magnetic moment and the saturation magnetic moment expected from the Slater-Pauling relation, as a function of temperature for both the ordered configuration and the disordered configuration, with the results of Dumpich *et al.* in the inset. We note the two main features which are the same as those found in the as-prepared and annealed film measurements: The Curie temperature and the saturation magnetization of the ordered configuration are larger than in the disordered configuration.

The increased Curie temperature is consistent with the behavior observed in other Fe-Ni ordered phases relative to their disordered counterparts, even though the chemical ordering temperature is lower than the magnetic ordering temperature. At 25 at. % Fe, the Curie temperature of ordered $FeNi_3$ is 954 ± 5 K, whereas in the disordered $Fe_{25}Ni_{75}$ alloy it is 871 ± 1 K.[19] In FeNi, the same effect can be observed in a meteoritic sample. The sample contains a chemically ordered phase and a disordered (or partially disordered) phase of the same composition, close to 50 at. % Fe. Based on Mössbauer measurements below 750 K, the ordering temperatures of the ordered and disordered alloys are 760 ± 10 K and 710 ± 20 K.[29] These results are also expected based on the Ising model parameters we use since the Fe-Ni magnetic bond energy $(|E^M_{\mathrm{FeNi}}|=|J_{\mathrm{FeNi}}\mu_{\mathrm{Fe}}\mu_{\mathrm{Ni}}/4\mu_B^2|=150$

K) is also larger than the magnetic bond energies for Fe-Fe ($|E^M_{\mathrm{FeFe}}|=39$ K) and Ni-Ni ($|E^M_{\mathrm{NiNi}}|=63$ K).

There is also a simple explanation for the difference in the saturation magnetizations of the as-prepared and annealed films. In agreement with the latent antiferromagnetism model of Invar magnetism[4] and the local moment frustration model of Rancourt and Dang,[8] recent electronic structure calculations on $\mathrm{Fe}_{64.8}\mathrm{Ni}_{35.2}$,[17] $\mathrm{Fe}_{65.6}\mathrm{Ni}_{34.4}$,[15] and $\mathrm{Fe}_{75}\mathrm{Ni}_{25}$ (Ref. 16) have shown that Fe atoms in an Fe-rich local environment tend to align opposite to the bulk magnetization. This is due to a negative exchange coupling J_{FeFe} between Fe moments and positive exchange couplings J_{FeNi} and J_{NiNi}, between Fe and Ni moments and between Ni moments, respectively. The Fe-Ni and Ni-Ni exchange bonds cause most moments to be aligned ferromagnetically but, when an Fe moment is surrounded by many Fe moments polarized in a given direction, it will align opposite to the magnetization direction. Yang Wang *et al.*[17] have, for example, calculated that when there are ten or more Fe NN's, a central Fe moment will align antiferromagnetically to the bulk magnetization direction. Within the Ising model and with the exchange parameters that we are using, an Fe moment surrounded by moments which are aligned in a given direction will align opposite to that direction when there are ten or more Fe NN's. It aligns ferromagnetically for nine or fewer Fe NN's. Recall now the distributions illustrated in Fig. 1. In the disordered configuration, 15% of the Fe atoms are surrounded by ten or more Fe atoms, and most of these (8.5% of all Fe moments at $T=0$ K) will align opposite to the magnetization direction, resulting in a reduced saturation magnetization. In the ordered configuration, there are no Fe atoms with more than eight Fe NN's, resulting in all Fe moments aligning in the magnetization direction. The ordered configuration produces a collinear ferromagnetic structure with a saturation magnetization consistent with the Slater-Pauling curve. Whereas the simple model described above does not account for slight spin canting or minor moment magnitude variation which will be different in the ordered and disordered configurations and whereas these features may cause differences between the saturation magnetizations of as-prepared and annealed films, it is clear that the principal difference comes from antiparallel alignment due to a combination of an antiferromagnetic exchange parameter J_{FeFe} and dramatically different distributions of local chemical environments. Indeed, recent electronic structure calculations[28] show that (i) near-Invar composition alloys are high moment alloys, and (ii) moment magnitude variations in going from *fully* chemically ordered high moment states to chemically disordered high moment states are less than 5%. The differences illustrated in Fig. 2, between *partially* ordered and chemically random states, are $\sim 20\%$.

Also related to the magnetism of the films are the extracted hyperfine field distributions from ^{57}Fe Mössbauer spectra. In the ordered configuration, since a collinear ferromagnetic structure occurs, only local chemical environments will yield different hyperfine field values. Since the distribution of local environments around the Fe probe atom is narrow, the hyperfine field distribution is also expected to be narrow. In the disordered configuration, the distribution of local environments is intrinsically broader, resulting in a broad distribution with a significant tail at low field values due to antiparallel spin alignments as well as spin canting. These are natural consequences of the transferred component of the hyperfine field in Fe-Ni.[11,27,31] The situation has also been examined by electronic structure calculations.[32]

Finally, before discussing the Invar effect, it is also worthwhile mentioning the difference between the lattice parameters of the as-prepared and annealed films and how these relate to chemical ordering. As observed by Robertson *et al.*,[33] in Fe-Ni alloys, the Fe-Ni NN distance is always smaller than Fe-Fe and Ni-Ni NN bond distances. Since chemical ordering favors Fe-Ni bonds, we expect chemically ordered structures to have smaller lattice parameters than their disordered counterparts, as is observed in the films analyzed by Dumpich *et al.* as well as in FeNi and FeNi_3. Chemically ordered FeNi has a slight tetragonal distortion, but its average RT lattice parameter is 3.5804 ± 0.0005 Å, as opposed to 3.5863 ± 0.0003 Å for the disordered alloy.[34,35] The RT lattice parameter of FeNi_3 is also slightly smaller than that of $\mathrm{Fe}_{25}\mathrm{Ni}_{75}$: 3.5522 ± 0.0007 Å versus 3.5544 ± 0.0002 Å.[19] The slight change in lattice parameter between the as-prepared and annealed films can thus be explained through the existence of chemical order.

C. Invar effect in chemically ordered and disordered $\mathrm{Fe}_{65}\mathrm{Ni}_{35}$ alloys

Having established that chemical ordering effects can cause the measured differences between the as-prepared and annealed films, we must also explain why both types of films exhibit an Invar effect. A model which is consistent with the measured properties of both films, as well as all other experimental observations in Fe-Ni alloys, is the local moment frustration model proposed by Rancourt and Dang.[8] It is based on a J_{FeFe} that is negative and on a $\partial J_{\mathrm{FeFe}}/\partial r$ that is large and positive. Both of the latter conditions and the correct magnitudes predicted by Rancourt and Dang have been corroborated by electronic structure calclulations of fcc iron.[36] Though applied specifically to explain the Invar effect in the disordered $\mathrm{Fe}_{65}\mathrm{Ni}_{35}$ alloy, we next show that the local moment frustration model also predicts an Invar effect in the ordered alloy.

Within a mainly collinear and ferromagnetic matrix of Ni and Fe spins, most Fe-Fe magnetic bonds are frustrated, since the spins are in a ferromagnetic configuration while $J_{\mathrm{FeFe}}<0$. The positive frustration energy U_f which results from the magnetic interaction is directly proportional to the difference between the number N_s of satisfied bonds and the number N_f of unsatisfied, or frustrated, bonds and to the magnetic exchange coefficient J_{FeFe} as

$$U_f=-\frac{\mu_{\mathrm{Fe}}^2}{4\mu_B^2}(N_f-N_s)J_{\mathrm{FeFe}}. \tag{3}$$

Assuming that $\partial J_{\mathrm{FeNi}}/\partial r$ and $\partial J_{\mathrm{NiNi}}/\partial r$ are negligible compared to $\partial J_{\mathrm{FeFe}}/\partial r$, the variation of frustration energy with the lattice parameter is

$$\frac{\partial U_f}{\partial r}=-\frac{\mu_{\mathrm{Fe}}^2}{4\mu_B^2}(N_f-N_s)\frac{\partial J_{\mathrm{FeFe}}}{\partial r}, \tag{4}$$

which is negative when Fe-Fe bonds are mostly frustrated ($N_f-N_s>0$) and $\partial J_{\mathrm{FeFe}}/\partial r$ is positive. An increase in the lattice parameter will thus reduce the frustration energy, at the expense of an increase in the chemical bonding energy. The equilibrium lattice position is thus higher than the equilibrium lattice parameter in the absence ($\partial J_{\mathrm{FeFe}}/\partial r = 0$) of a magnetovolume coupling. If $\partial J_{\mathrm{FeFe}}/\partial r$ is large enough, this expansion can be comparable to expected thermal lattice expansion. Since this expansion is related to the number of frustrated Fe-Fe bonds, it is directly related to the magnetization of the sample, and disappears at and above the Curie temperature where $N_s = N_f$. When compounded with the normal thermal expansion of the lattice, the gradual decrease with temperature of the frustration induced expansion causes a flattening of the thermal expansion curve. At 65 at. % Fe, the flattening is such that the net result is the anomalously low thermal expansion known as the Invar effect.

We have mentioned above that in the disordered configuration, not all Fe moments align in the direction of the bulk magnetization. In this configuration, $(N_f - N_s)/(N_f + N_s) \simeq 0.6$. In the ordered configuration, all Fe moments are aligned in the same direction and $(N_f - N_s)/(N_f + N_s) = 1.0$. However, the total number of Fe-Fe bonds depends on the populations of local chemical environments, which are characterized by the Fe NN distributions shown in Fig. 1, such that in the disordered configuration, there are more Fe-Fe bonds than in the ordered configuration. The Invar expansion due to frustration is thus expected to be of similar magnitude in both films and its temperature dependence is expected to cause a similar Invar effect in both the disordered and ordered configurations.

In order to better illustrate and quantify these points, we have performed constant temperature and zero pressure MC simulations[18] of $Fe_{65}Ni_{35}$ using an Ising model to describe the magnetism and three Lennard-Jones potentials to describe NN-only chemical interactions of Fe-Fe, Fe-Ni, and Ni-Ni pairs. The Lennard-Jones potentials were taken to have minima consistent with the cohesive energies used in the MC simulation of chemical order described above, and NN minimal energy distances corresponding to a Vegard's law-type behavior and consistent with experimental values ($d_{\mathrm{FeFe}} = 2.567$ Å, $d_{\mathrm{FeNi}} = 2.526$ Å, and $d_{\mathrm{NiNi}} = 2.485$ Å). When applied to pure fcc Ni and using the same physical parameters, our isothermal-isobaric MC simulation gives the same cell volume versus temperature curve as does the combined molecular dynamics and MC method of Grossmann and Rancourt.[38] The details are given elsewhere (unpublished) and Fig. 3 shows the resulting simulated thermal expansion curves for the ordered and disordered configurations with and without a magnetovolume coupling, $\partial J_{\mathrm{FeFe}}/\partial r$, along with the measured fractional volume expansion ($\Delta V/V$) in bulk $Fe_{64.5}Ni_{35.5}$ Invar.[37] Even though the magnetism of the $Fe_{65}Ni_{35}$ alloy is not exactly reproduced using an Ising model, this figure shows qualitatively how the Invar effect occurs in both the ordered and disordered configurations. The systematic difference between the values in the $\partial J_{\mathrm{FeFe}}/\partial r \neq 0$ paramagnetic state and the values at the same temperatures for the $\partial J_{\mathrm{FeFe}}/\partial r = 0$ case are real and are understood in terms of the combined effects of a nonquadratic interatomic potential and a nonzero magnetovolume coupling.[38]

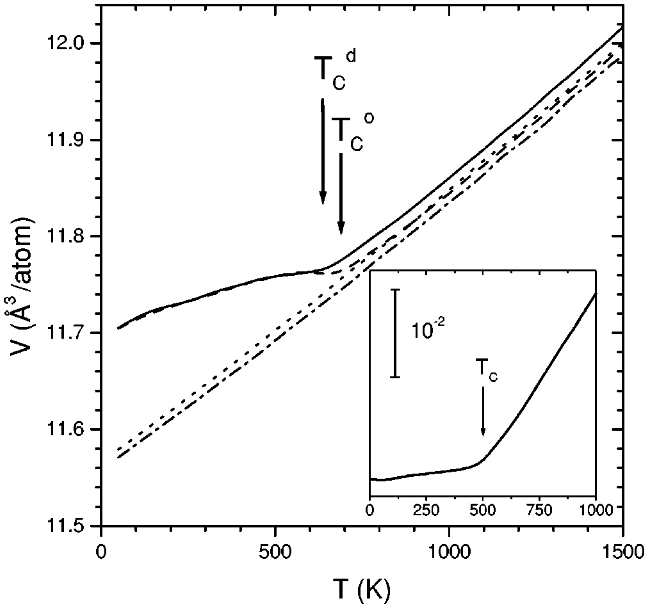

FIG. 3. Thermal average of the atomic volume as obtained by isothermal-isobaric ($P = 0$) MC simulations illustrating the effect of a large magnetovolume coupling parameter $\partial J_{\mathrm{FeFe}}/\partial r$. The solid and dotted curves correspond to the disordered configuration with $\partial J_{\mathrm{FeFe}}/\partial r = 1275$ K/Å and $\partial J_{\mathrm{FeFe}}/\partial r = 0$ K/Å, respectively. The dashed and dash-dotted curves correspond to the ordered configuration with $\partial J_{\mathrm{FeFe}}/\partial r = 1275$ K/Å and $\partial J_{\mathrm{FeFe}}/\partial r = 0$ K/Å, respectively. The Curie temperatures (T_C^o and T_C^d) of the two lattice configurations are indicated. Inset: Measured fractional volume expansion ($\Delta V/V$) in $Fe_{64.5}Ni_{35.5}$ Invar (Ref. 37).

IV. CONCLUSION

We have shown that the remarkable observations of Dumpich *et al.*,[9] who found as-prepared Invar composition ($Fe_{65}Ni_{35}$) thick films (200 nm) to exhibit Invar behavior (i.e., near-zero thermal expansion in a broad temperature range near RT) despite being collinear ferromagnets having saturation magnetizations that do not deviate from the Slater-Pauling curve, are explained by the presence of Fe_3Ni-type chemical order rather than by an ''absence of premartensitic effects'' as they originally proposed. By a careful examination of available data and by use of MC simulations of the physical properties associated with chemical ordering, magnetic ordering, and thermal expansion with magnetovolume coupling, we have shown that all of the observations of Dumpich *et al.*, for both as-prepared and annealed films (that recover bulk quenched Invar alloy behavior), are consistent with the effects of varying degrees of chemical order, which in turn are consistent with the sample preparation and treatment methods used.

This interpretation of the experimental observations of Dumpich *et al.* allows one to derive the full implications of their results. Contrary to the superficial conclusion that since exchange frustration causes moment noncollinearity that causes deviation from the Slater-Pauling curve and since such deviation is not required for Invar behavior then exchange frustration is not required for Invar behavior in $Fe_{65}Ni_{35}$, we find that exchange bond frustration persists in the collinear ferromagnetic state that is stabilized by chemical order and that it is a required feature for Invar behavior to occur in both chemically ordered and disordered $Fe_{65}Ni_{35}$

because it effectively changes the sign of the magnetovolume effect that arises from the large and positive magnetovolume coupling parameter ($\partial J_{\mathrm{FeFe}}/\partial r$) that is predicted by *ab initio* calculations,[36] in accordance with the local moment frustration model of Rancourt and Dang.[8] In other words, one must distinguish moment noncollinearity, which is one possible consequence of exchange bond frustration, from exchange bond frustration itself, which is the presence of exchange bonds that are not energetically satisfied. We are also able to make conclusive statements regarding several competing models for Invar behavior: (i) all models that rely on chemical or magnetic clusters or inhomogeneities must be ruled out since the as-prepared and annealed films of $Fe_{65}Ni_{35}$ are understood to have significantly different distributions of local chemical environments whereas they have similar Invar behaviors, (ii) the once predominant weak itinerant ferromagnetism model of Wohlfarth[3] must be ruled out because the as-prepared film of $Fe_{65}Ni_{35}$ is clearly a strong ferromagnet, with no deviation from the Slater-Pauling curve, and (iii) recent attempts to explain Invar behavior from $T=0$ K electronic structure calculations that argue that moment noncollinearity is essential in order to give the correct energy versus lattice parameter curve which in turn gives rise to the anomalously small thermal expansion[15] must also be seen to be incorrect.

Overall, we are able to explain all the observations concerning both chemically ordered and disordered $Fe_{65}Ni_{35}$ within the framework of the local moment frustration model of Rancourt and Dang.[8] This lends further support to the latter model, that was originally developed for quenched and chemically disordered Fe-Ni alloys, and to the view that $Fe_{65}Ni_{35}$ Invar is predominantly a high moment material in which the moment magnitude is closer to a high moment value than to a low moment value and is not significantly affected by changing temperatures, at the relevant temperatures of the Invar effect. This view is in opposition to all models that appeal to thermal excitation of a low moment state or to thermal stabilization of the low moment phase, as temperature is increased. The latter types of models can be shown to be incorrect for the case of $Fe_{65}Ni_{35}$ Invar.[39]

Finally, we note that this represents the most convincing evidence to date of Fe_3Ni-type chemical order in the Fe-Ni alloy system. Although theoretical calculations that assume a high moment electronic structure have predicted that Fe_3Ni should occur with an ordering temperature lower but comparable to that of $FeNi_3$,[26] it has not been previously observed for several reasons: (i) it has proved difficult to stabilize fcc $Fe_{75}Ni_{25}$ because of the martensitic transition to the bcc structure, (ii) at 75 at. % Fe, the low moment phase is more stable than the high moment phase, as predicted by *ab initio* calculations,[40] and (iii) its low value of the ordering temperature would presumably make it difficult to produce by ordinary thermal treatment methods, especially given the spinodal decomposition that is also believed to occur at near-Invar compositions.[23,41] Its existence in the as-prepared $Fe_{65}Ni_{35}$ film may constitute further evidence that Invar is predominantly a high moment material: It is possible that the greater density of conduction electrons in the low moment phase is associated with bonding energies that do not give rise to a strong preference for Fe-Ni bonds, as observed in the high moment fcc alloys.

---

*Corresponding author.
Electronic address: dgr@physics.uottawa.ca

[1] C. E. Guillaume, C. R. Hebd. Seances Acad. Sci. **124**, 176 (1897); Proc. Phys. Soc. London **32**, 374 (1920).

[2] R. J. Weiss, Proc. Phys. Soc. London **82**, 281 (1963); M. Matsui, K. Adachi, and S. Chikazumi, J. Appl. Phys. **51**, 6319 (1980); S. Chikazumi, J. Magn. Magn. Mater. **10**, 113 (1979).

[3] E. P. Wohlfarth, J. Magn. Magn. Mater. **10**, 120 (1979).

[4] A. Z. Menshikov, Physica B **161**, 1 (1989), and references therein; W. J. Carr, Jr., Phys. Rev. **85**, 590 (1952).

[5] For example, *Physics and Applications of Invar Alloys*, edited by H. Sato (Maruzen Company Ltd., Tokyo, 1978); M. Shiga, in *Materials Science and Technology*, edited by R. W. Cahn, P. Hasen, and E. J. Kramer (VCH, Weinheim, 1993), Vol. 3B, Part II, p. 159.

[6] C. Woolger, Mater. World **4**, 332 (1996); L. L. Harner, Advanced Materials and Process. **5**, 31 (1997); *The Invar Effect: A Centennial Symposium*, edited by J. Wittenauer (The Minerals, Metals & Materials Society, Warrendale, PA, 1997).

[7] E. F. Wassermann, Festkoerperprobleme **27**, 85 (1987); J. Magn. Magn. Mater. **100**, 346 (1991); V. L. Moruzzi, J. Magn. Magn. Mater. **161**, 99 (1989); Phys. Rev. B **41**, 6939 (1990); Solid State Commun. **83**, 739 (1992); E. G. Moroni and T. Jarlborg, Physica B **161**, 115 (1989); Phys. Rev. B **41**, 9600 (1990); E. F. Wassermann, in *Handbook of Magnetic Materials*, edited by K. H. J. Buschow (North-Holland, Amsterdam, 1990), Vol. 5, p. 237; B. Buchholz, E. F. Wassermann, W. Pepperhoff, and M. Acet, J. Appl. Phys. **75**, 7012 (1994).

[8] D. G. Rancourt and M.-Z. Dang, Phys. Rev. B **54**, 12 225 (1996).

[9] G. Dumpich, J. Kästner, U. Kirschbaum, H. Mühlbauer, J. Liang, and E. F. Wassermann, Phys. Rev. B **46**, 9258 (1992).

[10] C. G. Shull and M. K. Wilkinson, Phys. Rev. **97**, 304 (1955).

[11] J. Y. Ping and D. G. Rancourt, J. Magn. Magn. Mater. **103**, 285 (1992); D. G. Rancourt and J. Y. Ping, Hyperfine Interact. **69**, 497 (1991).

[12] G. Dumpich, E. F. Wassermann, V. Manna, S. Murayama, and Y. Miyako, J. Magn. Magn. Mater. **67**, 55 (1987).

[13] G. Dumpich, E. Becker, K. Schletz, W. Stamm, W. Keune, W. Kiauka, and S. Murayama, J. Magn. Magn. Mater. **74**, 237 (1988).

[14] E. F. Wassermann, G. Dumpich, U. Kirschbaum, and J. Liang, in *Proceedings of the International Conference on the Physics of Transition Metals 1992*, edited by P. M. Oppeneer and J. Kübler (World Scientific, London, 1992), Vol. 2.

[15] M. van Schlifgaarde, I. A. Abrikosov, and B. Johansson, Nature (London) **400**, 46 (1999).

[16] M. Schröter, H. Ebert, H. Akai, P. Entel, E. Hoffmann, and G. G. Reddy, Phys. Rev. B **52**, 188 (1995).

[17] Yang Wang, G. M. Stocks, D. M. C. Nicholson, W. A. Shelton, V. P. Antropov, and B. N. Harmon, J. Appl. Phys. **81**, 3873 (1997).

[18] D. W. Heermann, *Computer Simulation Methods in Theoretical Physics*, 2nd ed. (Springer-Verlag, Berlin, 1990).

[19] R. J. Wakelin and E. L. Yates, Proc. Phys. Soc. London, Sect. B **66**, 221 (1952).

[20] J. F. Petersen, M. Aydin, and J. M. Knudsen, Phys. Lett. **62A**, 192 (1977).

[21] J. Paulevé, D. Dautreppe, J. Laugier, and L. Néel, C. R. Hebd. Seances Acad. Sci. **254**, 965 (1962).

[22] L. J. Swartzendruber, V. P. Itkin, and C. B. Alcock, J. Phase Equilib. **12**, 288 (1991), specifically, Fig. 6, p. 296.

[23] J. I. Goldstein, D. B. Williams, J. Zhang, and R. Clarke, in *Physical Metallurgy of Controlled Expansion Invar-Type Alloys*, edited by K. C. Russell and D. F. Smith (The Minerals, Metals & Materials Society, Warrendale, PA, 1990).

[24] D. G. Rancourt, K. Lagarec, A. Densmore, R. A. Dunlap, J. I. Goldstein, R. J. Reisner, and R. B. Scorzelli, J. Magn. Magn. Mater. **191**, L255 (1999).

[25] P. S. Maiya and J. M. Blakely, J. Appl. Phys. **38**, 698 (1967).

[26] M. Z. Dang and D. G. Rancourt, Phys. Rev. B **53**, 2291 (1996).

[27] M. Z. Dang, Ph.D. thesis, University of Ottawa, 1996; M. Z. Dang, M. Dubé, and D. G. Rancourt, J. Magn. Magn. Mater. **147**, 133 (1995).

[28] P. James, O. Eriksson, B. Johansson, and I. A. Abrikosov, Phys. Rev. B **59**, 419 (1999).

[29] E. De Grave, R. E. Vandenberghe, P. M. A. De Bakker, A. Van Alboom, R. Vochten, and R. Van Tassel, Hyperfine Interact. **70**, 1009 (1992).

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

[31] M. Z. Dang and D. G. Rancourt, in *Conference Proceedings*, ICAME-95, edited by I. Ortalli (SIF, Bologna, 1996), Vol. 50, p. 367.

[32] H. Ebert, H. Winter, B. L. Gyorffy, D. D. Johnson, and F. J. Pinski, J. Phys. F: Met. Phys. **18**, 719 (1988).

[33] J. L. Robertson, G. E. Ice, C. J. Sparks, X. Jiang, P. Zschack, F. Bley, S. Lefebvre, and M. Bessiere, Phys. Rev. Lett. **82**, 2911 (1999).

[34] J. F. Albertsen, Phys. Scr. **23**, 301 (1981).

[35] E. A. Owen and E. L. Yates, Proc. Phys. Soc. London **49**, 315 (1937).

[36] R. F. Sabiryanov, S. K. Bose, and O. N. Mryasov, Phys. Rev. B **51**, 8958 (1995).

[37] M. Hayase, M. Shiga, and Y. Nakamura, J. Phys. Soc. Jpn. **30**, 729 (1973).

[38] B. Grossmann and D. G. Rancourt, Phys. Rev. B **54**, 12 294 (1996).

[39] K. Lagarec, D. G. Rancourt, S. K. Bose, B. Sanyal, and R. A. Dunlap (unpublished).

[40] I. A. Abrikosov, O. Eriksson, P. Soderlind, H. Skriver, and B. Johansson, Phys. Rev. B **51**, 1058 (1995).

[41] D. G. Rancourt and R. B. Scorzelli, J. Magn. Magn. Mater. **150**, 30 (1995); D. G. Rancourt and R. B. Scorzelli, *ibid.* **174**, 324 (1997).