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INVAR BEHAVIOR IN Fe–Ni ALLOYS IS PREDOMINANTLY A LOCAL MOMENT EFFECT ARISING FROM THE MAGNETIC EXCHANGE INTERACTIONS BETWEEN HIGH MOMENTS

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I argue that the main models that have been advanced to explain Invar behavior in Fe–Ni alloys (the original, classical, Invar system) can all be shown to be critically deficient, except one: The local moment frustration model of Rancourt and Dang (*Phys. Rev. B*, **54**, 12225, 1996). The latter model explains all the measured structural, magnetic, and magnetovolume features of the Fe–Ni alloys with 0–65 apc (atomic percent) Fe, based on the assumptions that these systems are predominantly high-moment in character at the temperatures of interest and that the Fe–Fe pairs have large inter-atomic separation dependencies of their magnetic exchange parameters. The large magnetovolume Fe–Fe couplings are understood (based on *ab initio* electronic structure calculations) as a precursor effect of the low-moment/high-moment (LM/HM) transition that has recently been observed to occur at larger Fe concentrations, as a continuous transition occurring in the range ∼65–75 apc Fe (Lagarec, Ph.D. thesis, 2001).

Keywords: Invar; Anti-Invar; Fe–Ni; Magnetovolume; Low-moment; Magnetism

1. INTRODUCTION

The Invar Problem, to uncover the main cause(s) of Invar behavior in classical $Fe_{65}Ni_{35}$ Invar, has not yet been solved to the general satisfaction of a majority of researchers in the field of magnetovolume effects (Sato, 1978; Shiga, 1994). This is evident by the large variety of quite different proposed models and the large variety of opinions about which features of the observed behaviors of Fe–Ni alloys are "essential" and which are "ancillary". Indeed, it was obvious also at this symposium.

In this context, it is useful to proceed by elimination, since several proposed models can be shown to clearly contradict the most direct interpretations of experimental observations. Only one valid contradiction is needed to invalidate a given model. I draw attention to a select number of recent results and publications that deserve special acknowledgement because they provide pivotal arguments. A valid model must then explain all the observed features and must be general enough to elucidate the behaviors of other alloy systems and to provide some predictive insight.

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2. CRITICAL EXAMINATION OF PROPOSED MODELS FOR INVAR

I examine the following models and classes of models (these will be referred to either by name or as model-A, etc.):

(A) the weak itinerant ferromagnetism model of Wohlfarth (1979),
(B) the ionic two-γ-state model of Weiss (1963); Matsui *et al.* (1980); Chikazumi (1979),
(C) the latent antiferromagnetism model of Menshikov (1980) and Carr (1952),
(D) models based on the proposition that the Invar effect arises directly from the proximity in energy, compared to $k_B T$ at room temperature, of LM and HM electronic structures, by virtue of the LM phase having a smaller equilibrium volume,
(E) models based on a necessity for chemical clustering or local environment effects or some degree of long range or short range chemical order,
(F) models, such as expressed in particular in a very recent article by van Schilfgaarde *et al.* (1999), that are based on the necessity for a non-collinear spin structure, and
(G) the local moment frustration model of Rancourt and Dang (1996).

One recent article, by Lagarec and Rancourt (1999), allows one to eliminate several of the above models and is therefore worth describing. Lagarec and Rancourt reexamined the remarkable experimental results of Dumpich *et al.* (1992) who synthesized face centered cubic (FCC) $Fe_{65}Ni_{35}$ samples that exhibited the usual Invar effect (a very small thermal expansion coefficient in the neighborhood of room temperature) but did not exhibit the usual deviation from the Slater–Pauling curve. That is, these samples, contrary to ordinary quenched $Fe_{65}Ni_{35}$ Invar, were collinear ferromagnets having the saturation magnetization predicted by Slater–Pauling behavior. Lagarec and Rancourt showed that these and other observations are explained by the presence of Fe_3Ni-type chemical order in the novel samples of Dumpich *et al.* This is very significant because it establishes that the Invar behavior of FCC $Fe_{65}Ni_{35}$ does *not* depend on either a non-collinear spin structure or the degree of long range or short range chemical order or a deviation from the Slater–Pauling curve. Consequently, models A, E, and F *must* be wrong.

Model-C is the precursor to model-G in that both are HM local moment models. The main feature of model-C is that non-collinear spin arrangements were proposed to be the main causes of the observed magnetic anomalies. In model-C, the magnetovolume anomalies were then explained as arising from a large Fe–Fe magnetovolume coupling (i.e., inter-atomic separation dependence of the exchange) that needed to be postulated *ad hoc*. All of this is reasonable, and consistent with experimental observations, but the required sign of the magnetovolume coupling parameter was opposite to that recently obtained (Sabiryanov *et al.*, 1995) by *ab initio* electronic structure calculations. Rancourt and Dang (model-G) recognized the importance of magnetic exchange bond frustration in that it effectively changes the sign of the required magnetovolume coupling parameter. Note that, in this context, one must carefully distinguish magnetic exchange bond frustration (in which the exchange bonds are not energetically satisfied) from one of its possible consequences: non-collinear spin structures.

Model-B is the pre-*ab initio* precursor of model-D. These two models are often linked conceptually although it is important to clearly distinguish them. Model-B is a local ionic state model whereas model-D is based on or inspired by *ab initio* electronic structure calculations (applicable only at $T = 0\,K$) that find either LM or HM extended phases to be stabilized, depending on the value of the imposed lattice parameter.

Model-B postulates that the Fe ions have low-spin and high-spin states with energies that are not too different from thermal energy at room temperature, for excitations from one to the other to occur. There is no direct experimental evidence for the existence of two such states of Fe ions in Fe–Ni alloys, as should be easily observed, for example, by ^{57}Fe Mössbauer spectroscopy. Whereas model-B offers explicit mean field calculation methods for making quantitative comparisons with experiment, expressions of model-D usually do not but are more based on the general (and widespread) idea (Wassermann, 1987, 1990, 1991; Moruzzi, 1989, 1992a,b; Moroni and Jarlborg, 1989, 1990; Buchholz et al., 1994; Mohn et al., 1989, 1991; Hoffmann et al., 1993; Entel et al., 1993; Schröter et al., 1995) that the Invar effect is a contraction (as temperature is raised) that directly arises from stabilization of or thermal excitation towards the LM phase that is predicted to occur at smaller lattice parameter values in ($T = 0$ K) ab initio calculations.

So, we are left with two main contenders: Local moment models (models C and G) and LM/HM models (models B and D). How can these two be resolved? I offer the following arguments that LM/HM models must be abandoned in favor of the local moment frustration model of Rancourt and Dang. The reader should be warned that this is not to say that a LM/HM transition does not occur in the Fe–Ni system, nor that it does not have significant measurable effects, nor that the same electrons that cooperate to cause a LM/HM transition (at larger Fe concentrations) do not also cause the particular conditions (large magnetovolume coupling parameter and bond frustration) that validate the local moment frustration model (at near Invar and smaller Fe concentrations). The point, however, is that classical $Fe_{65}Ni_{35}$ Invar is predominantly a HM alloy with strong magnetic exchange interactions, although it is at a composition where the continuous LM/HM transition has partially occurred (Lagarec, 2001; Lagerec et al., 2001). By comparison, consider that the electronic structure is also the predominant factor determining the presence of the martensitic transition (FCC to body centered cubic structure) that occurs at higher Fe concentrations, as the FCC component undergoes a LM/HM transition (Lagarec, 2001) and that this structural transition is not believed to play a direct role in Invar behavior.

3. WHY LM/HM MODELS FOR INVAR BEHAVIOR SHOULD BE ABANDONED

The LM/HM proposal can be expressed as follows: "LM and HM phases are calculated to have differences in energy per atom that are comparable to $k_B T$ at room temperature. Therefore, thermal excitation from the larger volume HM phase to the smaller volume LM phase, as temperature is increased, can explain the Invar effect." This is a popular current picture of Invar, that is repeated in various forms in many published articles (Wassermann, 1987, 1990, 1991; Moruzzi, 1989, 1992a,b; Moroni and Jarlborg, 1989, 1990; Buchholz et al., 1994; Mohn et al., 1989, 1991; Hoffmann et al., 1993; Entel et al., 1993; Schröter et al., 1999). The main problems with this view are as follows.

First, the electronic structure calculations relate to an extended uniform phase, not a local ionic state. Therefore, the correct energy of excitation must relate to a certain volume of the excited phase in a matrix of the lower energy phase, with proper interfacial energy term. Also, as it turns out, more refined ab initio calculations that allow local environment effects and non-collinear spin structures find that separate LM

and HM local minima of the energy do not occur but that, instead, one obtains a continuous transition from LM character to HM character, as the lattice parameter is increased (van Schilfgaarde et al., 1999; Akai and Dederichs, 1993; Wang et al., 1997; James et al., 1999). The relation to the original two-γ-states model now becomes tenuous indeed.

Secondly, there has been experimental evidence since 1989 (Rancourt et al., 1989) that LM and HM phases can coexist as separate extended phases, in a broad composition range of Fe–Ni including $Fe_{65}Ni_{35}$ Invar. This is further supported by compelling results from Fe–Ni-bearing meteorites (Rancourt and Scorzelli, 1995; Rancourt et al., 1999), in which separate Fe–Ni LM phases (antitaenite) are clearly identified and shown to be quite different from the coexisting Fe–Ni HM phases (taenite and tetratae-nite). Taken together, these experimental results imply that LM and HM phases in the Fe–Ni system are separate extended phases that are mainly stabilized by composition and by microstructural constraints and that cannot easily be thermally transformed one into the other.

Thirdly, one must contend with the undeniable experimental observation that Invar behavior, in the entire FCC Fe–Ni series, is intimately linked to the alloys' (HM) ferromagnetism. It sets in at the Curie points, on decreasing the temperature, and it occurs over a broad composition range that includes the unambiguously HM more Fe-poor alloys. In addition, the paramagnetic states (above the Curie points) have normal thermal expansions and large magnetic moment magnitudes. The Invar effect is not confined to $Fe_{65}Ni_{35}$ but occurs continuously over a broad concentration range of the FCC alloys ($\sim$25–70 apc Fe), yet the alloys in the range 0 to $\sim$ 60 apc Fe are unambiguously pure HM alloys, with moment magnitudes of 2.8 μ_B/Fe-atom and 0.6 μ_B/Ni-atom. In a LM/HM picture of Invar (models B and D) one must add ad hoc modifications or proposals in order to couple the calculated Invar behavior to the underlying ferromagnetism whereas in local moment models (models C and G) this coupling occurs naturally because the magnetovolume effect arises from the local moment interactions and directly depends on the degree of magnetic order at a given temperature.

Fourthly and perhaps most importantly, all low-spin/high-spin and LM–HM pro-posals require the Invar effect to be a contraction relative to normal (HM non-magnetovolume) behavior whereas the measured Invar effect is an expansion. It is an expansion both relative to the paramagnetic behaviors of all the magnetovolume-active FCC Fe–Ni alloys, when the above Curie point normal thermal behaviors are extrapolated down to lower temperatures, and relative to the Vegard's law (Vegard, 1928; Thorpe et al., 1991) extrapolation in composition (at fixed temperature below all Curie points) of the lattice parameters from the non-magnetovolume-active alloys (0–25 apc Fe) to the compositions of magnetovolume-active alloys, as recently shown by Lagerec (2001) and Lagerec et al. (2001). This is the experimental proof that LM/HM models are wrong. The extrapolated normal behavior from the HM paramag-netic state temperatures of alloys that are unambiguously purely HM in character shows the low temperature magnetovolume deviation to be an expansion relative to this normal behavior. An expansion is incompatible with the proposed LM/HM mechanism that relies on stabilization or excitation towards a smaller volume phase in the magnetovolume active region.

One could argue that the paramagnetic state of $Fe_{65}Ni_{35}$ Invar is not a normal HM state and that, therefore, the LM/HM mechanism is not incompatible with the

temperature extrapolation but this would leave three problems: (1) One would need different magnetovolume mechanisms for near Invar compositions and all unambiguously HM FCC Fe–Ni alloys that are magnetovolume active, whereas the degree of magnetovolume strength varies continuously with composition. (2) One would still need to explain the above mentioned expansion with respect to the low Fe concentration Vegard's law, again observed in a broad composition range spanning unambiguously HM alloys (Lagarec, 2001; Lagerec *et al.*, 2001). (3) One would need to reconcile this view with both direct moment magnitude measurements in $Fe_{65}Ni_{35}$ at high temperature that find only moderately reduced moments (Shull and Wilkinson, 1955; Collins *et al.*, 1962; Hatherly *et al.*, 1964; Ishikawa *et al.*, 1979; Brown *et al.*, 1989) and the recent isomer shift measurements of Lagarec (2001) and Lagerec *et al.* (2001) at temperatures across the Curie point in $Fe_{65}Ni_{35}$ that show only a moderate change in electronic structure with increasing temperature. Invar ($Fe_{65}Ni_{35}$) is not a purely HM alloy but it must now be understood to be predominantly a HM alloy, on the HM edge of the predominantly composition controlled LM/HM transition.

4. LOCAL MOMENT FRUSTRATION MODEL, ITS *AB INITIO* JUSTIFICATION, AND ITS LIMITS

In a series of papers (Dang *et al.*, 1995; Dubé *et al.*, 1995; Dang and Rancourt, 1996; Grossmann and Rancourt, 1996) culminating in the description of the local moment frustration model (Rancourt and Dang, 1996), we have shown by various mean field theory and Monte Carlo calculations that a simple HM local moment model, with fixed moment magnitudes on Fe and Ni, three constant exchange parameters for Fe–Fe, Fe–Ni, and Ni–Ni pairs, and one non-zero constant magnetovolume coupling parameter, $J'_{Fe–Fe} = \partial J_{Fe–Fe}/\partial r$, for Fe–Fe pairs, can reproduce the composition and temperature dependencies of all the physical properties of interest: saturation magnetization and deviation from the Slater–Pauling curve, thermal expansion, Curie point, spontaneous volume change, paraprocess high-field magnetic susceptibility, chemical order-disorder effects, bulk modulus, magnetic specific heat, etc. This simple model, with only four adjustable parameters, gives good qualitative agreement and at worst correct orders of magnitudes in the entire range 0 to ~ 65 apc Fe and at all relevant temperatures, provided the Fe–Ni and Ni–Ni exchange interactions are relatively large and positive (i.e., ferromagnetic), the Fe–Fe exchange interaction is somewhat smaller and negative (antiferromagnetic), and $\partial J_{Fe–Fe}/\partial r$ is large and positive ($+10^4$ K/Å, with the Hamiltonian used by Rancourt and Dang (1996)).

The negative Fe–Fe exchange parameter causes some spin non-collinearity, which is the main cause of the deviation from the Slater–Pauling curve at lower Fe concentrations. The great majority of Fe–Fe exchange bonds, however, are energetically frustrated and contribute to the bulk ferromagnetic moment. This frustration changes the sign of the magnetovolume effect by causing the positive $\partial J_{Fe–Fe}/\partial r$ to produce an expansion, as required. This is a key point, the spin structure need not be non-collinear but the Fe–Fe exchange bonds must be predominantly frustrated (by the dominant Fe–Ni and Ni–Ni ferromagnetic interactions) to allow the positive $\partial J_{Fe–Fe}/\partial r$ to produce the correct sign of the magnetovolume effect.

At this stage, the local moment frustration model was fully developed, and compelling in its simplicity, but two problems remained: (1) there was no fundamental

justification for the values of the exchange parameters and of $\partial J_{\text{Fe–Fe}}/\partial r$ that were required to make it all work, and (2) the model predictions gradually broke down as the concentration was increased above ~ 65 apc Fe. Both of these problems have now been resolved. Although not published in relation to magnetovolume effects or Invar behavior, the paper by Sabiryanov *et al.* (1995) reported the first *ab initio* calculations of the Fe–Fe exchange and its inter-atomic separation (i.e., lattice parameter) dependence for FCC iron (their Fig. 6). We noticed this paper by accident several years after its publication and found that at the lattice parameter value where the Fe–Fe exchange had the correct value (20 K, converted to the Hamiltonian used by Rancourt and Dang (1996)), the derivative, $\partial J_{\text{Fe–Fe}}/\partial r$, also had the correct value. At this value of the lattice parameter, the model FCC iron system had not undergone its LM/HM transition and was in a clearly HM state, near the HM edge of the transition region, see Fig. 6 of Sabiryanov *et al.* (1995). Indeed, Fig. 6 of Sabiryanov *et al.*'s paper is probably the single most important published *ab initio* result with regards to explaining Invar behavior in Fe-rich FCC alloys, although no mention of Invar is made in it.

The second problem, regarding degradation of the local moment frustration model above ~ 65 apc Fe, can now also be understood. A composition driven LM/HM transition does occur in the FCC Fe–Ni system, as first predicted by Abrikosov *et al.* (1995) (although they incorrectly claimed that it directly caused the Invar effect, via the LM/HM mechanism (model-D above)) and as first observed only very recently by Lagarec (2001) and Lagerec *et al.* (2001). This transition is not taken into account in the local moment models that use constant moment magnitudes and constant interaction parameters. The degree of disagreement between local moment model predictions and measurements, at large Fe concentrations, can therefore be taken as a rough measure of the extent to which the system has evolved towards the LM state, in a continuous transition that starts as the concentration exceeds ~ 65 apc Fe. Classical $Fe_{65}Ni_{35}$ Invar must be interpreted as having a small amount of LM character while being predominantly HM in nature. Its Invar effect is a local moment effect. Indeed, the direct LM/HM contribution to its magnetovolume effect must have an opposite sign to its dominant local moment contribution and serves to diminish it somewhat.

5. CONCLUSION

In the author's opinion, as outlined above, the Invar problem is now solved. Significant further improvements in understanding and intellectual satisfaction will only come with the development of adequate non-zero temperature *ab initio* calculations that can handle all the required realistic features that, at present, are modelled phenomenologically and to a high degree of realism by local moment models. Our main concluding points are as follows.

(1) The Invar effect in Fe–Ni and probably all Fe-rich FCC alloys is predominantly a HM local moment effect arising from inter-moment exchange and magnetovolume interactions, as described in the HM local moment frustration model of Rancourt and Dang (1996) (model-G in our above list). In particular, this model explains both the broad range in compositions over which an Invar effect occurs and the fact that the effect is intimately linked to the spontaneous ferromagnetism.

(2) The Invar effect is an expansion, relative to normal (HM non-magnetovolume) behavior, not a contraction as would be required by all LM/HM mechanisms for Invar behavior. This invalidates models B and D in our above list.

(3) The weak itinerant ferromagnetism model, the models based on a necessity for chemical clustering or local environment effects or some degree of long range or short range chemical order, and the models that are based on the necessity for a non-collinear spin structure (models A, E, and F) are rigorously ruled out, based on the recent work of Lagarec and Rancourt (1999).

(4) Proximity of the LM/HM transition gives rise to the right combination of Fe–Fe exchange and magnetovolume interactions, as precursor effects of the transition and its associated significant loss of moment magnitude. That is, composition-driven changes in the electronic structure of the FCC alloys manifest themselves first as unusual interaction parameters, followed by moment magnitude loss and continued changes in the interaction parameters, as Fe concentration is increased.

(5) Non-collinear spin structures are not an essential feature for Invar behavior, not even in Fe–Ni. They are only a possible manifestation of the Fe–Fe exchange bond frustration that, in Fe–Ni, is an essential feature for Invar behavior. Otherwise, the predicted positive coupling could not produce the required expansions, relative to normal HM behavior.

(6) As pointed out by Lagarec (2001) , although it does not in Fe–Ni, Invar behavior could possibly arise without Fe–Fe exchange bond frustration in other FCC Fe-based alloys. According to our interpretation of the results of Sabiryanov et al. (1995) (their Fig. 6), this would occur further away from the LM/HM transition, on the HM side, where the Fe–Fe exchange is ferromagnetic and the magnetovolume coupling is still positive (although smaller than in the near transition region). With ferromagnetic bonds, they need not be frustrated (and would not be) to produce an expansion, although such a system would have a smaller magnetovolume effect because it would not be taking advantage of the exchange slope that is largest near the LM/HM transition, see Fig. 6 of Sabiryanov et al. (1995).

(7) The LM/HM transition is much more sensitive to composition than it is to temperature. Nonetheless, high temperatures do induce a small amount of migration towards the LM phase in $Fe_{65}Ni_{35}$ Invar due to loss of HM stabilization from the loss of HM magnetic order, although it remains predominantly high moment at all temperatures of interest (Lagarec, 2001; Lagerec et al., 2001). In this context, we must understand temperature as driving the system along a LM/HM continuum of homogeneous phases, depending on the concomitant effects of magnetic order, chemical order, moment orientational entropy, thermal expansion, etc. For example, very Fe-rich FCC Fe–Ni alloys that have LM ground states are found to evolve towards the HM phase as temperature is increased (Lagarec, 2001). This gives rise to the so called anti-Invar effect (Acet et al., 1994a,b; Uhl and Kübler, 1997). So, anti-Invar behavior is a direct manifestation of the LM/HM instability but Invar behavior is not.

(8) The local moment frustration model (model-G) correctly predicts the influences of chemical order on the magnetic, thermal, and magnetovolume properties of HM FCC Fe–Ni alloys (0–65 apc Fe), with no free parameters (Rancourt and Dang, 1996; Lagarec and Rancourt, 1999; Dang et al., 1995; Dubé et al., 1995; Dang and Rancourt, 1996; Grossmann and Rancourt, 1996). This represents significant predictive power that no other quantitative model of Invar behavior has achieved.

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