RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 41, NUMBER 13 1 MAY 1990

Calculation of Invar anomalies

E. G. Moroni
Institut Romand de Recherche Numérique en Physique des Matériaux (IRRMA), 1015 Lausanne, Switzerland

T. Jarlborg
Departement de Physique de la Matière Condensée, Université de Genève, 1211 Genève 4, Switzerland
(Received 6 December 1989)

We present a thermodynamic two-state model based on energy-band results at $T=0$ K and on a Debye approximation of the phonon contribution to the free energy in order to calculate various Invar anomalies. The band results for some Fe-based systems suggest that the nonmagnetic and ferromagnetic total energies are almost degenerate and that Invar behavior occurs when the average number of electrons per atom is near 8.5. Our model invokes fluctuations between the ferromagnetic and nonmagnetic states at equal volume and does not invoke large volume fluctuations.

The so-called Invar alloys, characterized by invariant thermal expansion up to room temperature, have been of technological importance for a long time.[1] In recent years there have been theoretical efforts for a microscopic understanding of the mechanisms behind the Invar behavior.[2-6] The early model of Weiss proposed that a transition from a ferromagnetic ground state to an antiferromagnetic excited state at increased temperatures leads to the Invar effect.[4] Electronic structure calculations have established the closeness between nonmagnetic (NM) and ferromagnetic (FM) states in Fe_3Ni (Refs. 2 and 5). In the present work we first determine the total energies of some Invar systems and show, subsequently, that thermal fluctuations between the FM and NM states at the *same volume* (other magnetic configurations have not been studied here) produce several typical Invar properties. Our thermodynamic model is valid for temperatures lower than the temperature at which the magnetic moment starts to disorder.

The electronic structure and total energies are calculated using the linear-muffin-tin-orbital method[7] together with local-spin-density (LSD) potential.[8] Most LSD calculations[9] give fcc NM as the ground state of pure iron, instead of the experimentally found bcc FM state, while the LSD band structure results of Moruzzi *et al.*[10] give bcc FM as the ground state. However, here we consider only configurations of the *same structure* (fcc) and the LSD approximation should be more reliable. The calculations are done for ordered Fe_3Ni in Cu_3Au structure. The fact that Fe_3Pt exists and has Invar behavior both as ordered and disordered phases[1] shows that disorder is not essential for the Invar behavior. Our results of the total energies for the NM and FM states[5] calculated for a large range of lattice constants have been fitted to Murnaghan's equation of state.

In Fig. 1 we show our calculated total energies of Fe_3Ni as a function of the radius of the Wigner-Seitz cell. As shown, we find a FM ground state but the energy difference between the two minima is very small ($\sim$0.5 mRy/atom) (FeNi is found to have larger separation, about 7 mRy/atom).[2,5] The two states have slightly different equilibrium lattice constants and different bulk moduli. fcc Fe_3Ni exhibits a large magnetic Grüneisen coefficient. The magnetic moment (M), the hyperfine field (H), and their pressure derivatives have been calculated for fcc-ordered Fe-Ni systems at several lattice constants and are given in Table I. The calculations show that the pressure derivatives are indeed largest near the Invar composition as in Fe_3Ni. Quantitatively, the calculated values agree well with experimental results on $Fe_{68.5}Ni_{31.5}$ at 4.2 K.[11]

The most known Invar anomalies are temperature dependent and they have been investigated in this work in terms of a two-state thermodynamic model combined with the band results at $T=0$ K. Theoretical models of the Invar behavior often involve fluctuations between the total-energy minima of the FM and NM states.[12] Alternatively, we consider magnetic fluctuations between the two states occurring at equal volume in order to avoid the problem of having regions of different volume coexisting in the solid (it would cause structural instabilities, melting, etc.). Further, since the two states differ in electronic structure, it is likely that fluctuations between them follow an electronic time scale, i.e., they are more likely to be magnetic (rapid) rather than accompanied by (slow) volume or structure modifications. This means in Fig. 1

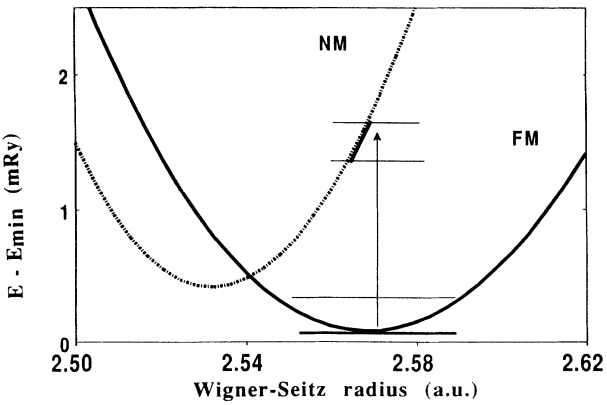

FIG. 1. Calculated total-energy curves (in mRy/atom) of nonmagnetic and ferromagnetic states for fcc Fe_3Ni in the Cu_3Au structure as a function of the Wigner-Seitz radius. The magnetic fluctuation is represented schematically by the arrow.

TABLE I. Calculated moments M, hyperfine fields H, and logarithmic pressure derivative of the hyperfine field and magnetic moment per atom for ordered fcc Fe, Fe_3Ni, and FeNi systems. In $Fe_{65}Ni_{35}$ and $Fe_{68.5}Ni_{31.5}$ at 4.2 K the experimental values (Ref. 11) of the pressure derivatives of M and H vary from -4.4 to -15 (Mbar)$^{-1}$. Our calculations confirm the experimental observation of a large magnetic Grüneisen coefficient near the Invar range.

	Fe (fcc)	$NiFe_3$		NiFe
Lattice constants (a.u.)	6.8	6.58	6.34	6.60
M (μ_B/atom)	2.45	1.37	0.26	1.43
Hf (kG)	−399	−257	−55	−304
$\frac{\delta \ln M}{\delta P}$ (Mbar)$^{-1}$	−0.48	−4.25	−10.06	−0.72
$\frac{\delta \ln H}{\delta P}$ (Mbar)$^{-1}$	−0.56	−3.72	−7.87	−0.74

that we exclude transitions which are not vertical, since such fluctuations would require an additional energy to make up for elastic or other energies confined in some kind of domain walls between the regions of different volumes. We assume that nearly "vertical" transitions are possible between FM and NM states without passing a high-energy barrier and that some scattering in energy ΔE around the two states is allowed, as is indicated by the arrow and the "energy windows" in Fig. 1. The quantity ΔE determines how many FM and NM states are accessible in the fluctuations (see later). As long as the energy window ΔE is small in comparison to the energy of the fluctuations $E^{NM}-E^{FM}$ (arrow), we can approximately reduce the problem of all transitions of different weights between FM and NM states to a problem of a transition between one FM and one NM state which have weights given by the number of states within ΔE. In other words, we let ΔE determine the range of volume fluctuation. However, with the volume strain $\Delta V/V$ of about 2%, which is realistic for normal materials at room temperature,[13] one is well below the fluctuations between the total-energy minima. This defines ΔE for the FM ground state at about 0.2 mRy/atom. (With this ΔE the NM excited state has smaller volume fluctuations since its total-energy curve is steeper in the region of interest). In short, the volume fluctuations due to thermal disorder are not considered to be more important than for normal materials and their effects are averaged out to give the proper weights in a two-state model. The free energy for such a two-state Invar system is approximately given by the sum of the total electronic free energy and the free energy of Debye lattice vibrations. The phonon energy and entropy are functions of the Debye temperature Θ_D (Ref. 14) in this approximation. This quantity can be determined from the bulk modulus (assuming that the high-q phonons scale as the low-q phonons) which, in turn, is calculated directly from the band results. The total energy for given V and T is expressed as the sum of the total energy of the magnetic ground state and the nonmagnetic excited state

$$E(V,T)=\sum_{i}^{NM\,FM} E^i(V)p_i(T,V,\Delta V)\,. \tag{1}$$

The populations of the NM or FM state are given by

$$p_i(T,V,\Delta V)=b_i(T,V)N_i(V,\Delta V)\,, \tag{2}$$

where $b_i(T,V)$ is the Boltzmann factor and where $N_i(V,\Delta V)$ is the number of states within a window ΔE around the value of the total-energy E_i. N_i can be related to pressure or volume fluctuations since it corresponds to including states which fluctuate around the averaged state. As mentioned above we use a normal volume strain of 2% at all T which corresponds to $\Delta P=(\Delta V/V)B(V)$ of about 30 kbar. The variation of the bulk modulus of the mixed system has been approximated via the relation

$$B(V,T)=\sum_{i}^{NM\,FM} B^i(V)p_i(T,V,\Delta V)\,, \tag{3}$$

i.e., no volume derivative of p_i is taken into account. The total free energy of the Invar system is minimized with respect to the volume at different temperature intervals in order to find the equilibrium volumes.

The calculated curve $\alpha(T)$ and $B(T)$ along with experimental data[15,16] are shown in Fig. 2 for Fe_3Ni. The calculated thermal expansion coefficient is strongly reduced

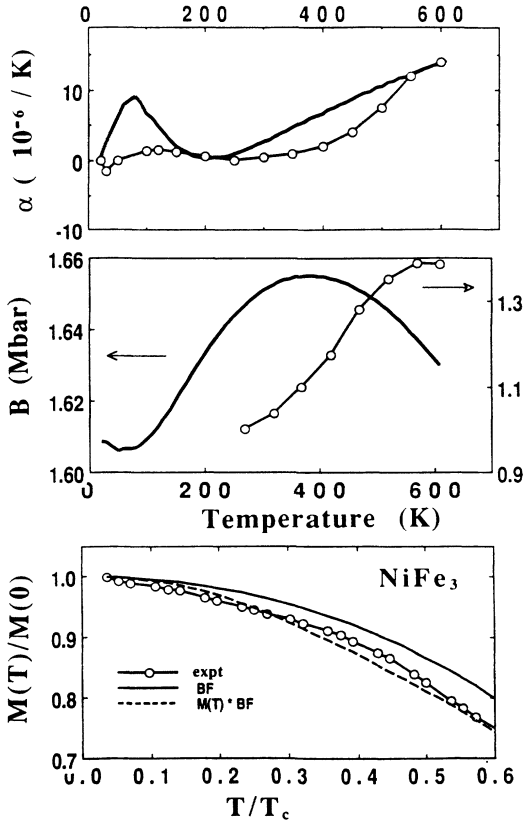

FIG. 2. (a) Temperature dependence of the calculated thermal expansion coefficient and (b) bulk modulus of ordered fcc Fe_3Ni. The two calculated curves (solid lines) are compared with experimental data (open dots) (Refs. 15 and 16) for an $Fe_{65}Ni_{35}$ Invar alloy. (c) Calculated relative spontaneous magnetization $M(T)/M(0)$ vs the relative temperature T/T_c ($T_c=560$ K) of ordered fcc Fe_3Ni in comparison with the Brillouin function (BF) and the experimental data for $Fe_{65}Ni_{35}$ (taken from Ref. 17).

(compared to the normal behavior) for T less than about room temperature and we obtain good agreement with experiment. Local-density approximation calculations predict too large bulk modulus for separate NM and FM states and therefore the bulk modulus of the fluctuating system is not quantitatively comparable with experiment, although the temperature dependence of B has a similar shape. Namely, at $T=0$ K, B is determined by the rather soft FM compressibility, while at larger T the NM state, having larger B,[5] becomes populated. Another characteristic of Invar property is the rapid decrease of the magnetic moment with temperature. Figure 2 shows the Brillouin function, the calculated relative magnetization for Fe_3Ni, and the experimental data for $Fe_{65}Ni_{35}$.[17] We find that the decrease of the magnetization is more rapid compared to the normal behavior of the ferromagnet (following the Brillouin function) since at higher temperature the NM state gradually becomes occupied. The behavior of the hyperfine field H is different. Experiments show that there is a dominant high-field peak which becomes broadened with increasing temperature.[18] The intensity decreases somewhat at higher T and other zero or low-field peaks appear. This behavior can be understood from the coexisting FM and NM states in which the relative occupations change with temperature. On the other hand, there is a strong pressure variation of hyperfine field and magnetic moment which also is found from the calculations (see Table I).

A further qualitative indication of a mixture of two states at higher T is found from spin-resolved photoemission.[19] A mixture of our calculated FM and NM density of states (DOS) following the occupations defined in Eq. (2) follows very well the experimental results for Fe_3Pt in Ref. 19. A similar analysis was done using Fe (fcc) DOS (Refs. 19 and 20) which both agree well with the experiments in Ref. 19. An alternative analysis based on disordered local-moment models is also able to produce the characteristic DOS structures without invoking a two-state model.[21] Therefore, comparisons with photoemission data do not seem to separate the different models.

In conclusion, our T-dependent results are interpreted as consequences of the magnetic fluctuations between low-energy FM state and high-energy NM state, without invoking large volume fluctuations (such as fluctuations between the total-energy minima[12]). This allows a qualitative explanation of Invar properties for T up to about room temperature. Calculated total-energy curves for fcc $Fe_xCo_{(1-x)}$ show small energy separation at $x=0.5$ and the same behavior is found for Fe_3Pt assuming the ordered Cu_3Au lattice, which confirm that the Invar behavior of Fe-based fcc alloys occurs when the number of electrons per atom is near 8.5. More detailed results of our calculation for several Fe-based Invar systems will be published elsewhere.

We acknowledge useful criticism and discussions with Professor S. Steinemann, Professor M. Peter, Dr. P. Renaud, and B. Barbiellini. This work was supported in part by the Swiss National Science Foundation under Grant No. 20-5446.87.

[1]E. F. Wasserman, Phys. Scr. **T25**, 209 (1989); Yoji Nakamura, IEEE Trans. Magn. **12**, 278 (1976).

[2]A. R. Williams, V. L. Moruzzi, C. D. Gelatt, Jr., and J. Kübler, J. Magn. Magn. Mater. **31-34**, 88 (1983); A. R. Williams, V. L. Moruzzi, C. D. Gelatt, Jr., J. Kübler, and K. Schwarz, J. Appl. Phys. **53**, 2019 (1982).

[3]J. Kaspar and D. R. Salahub, Phys. Rev. Lett. **47**, 54 (1981); P. Entel, M. Schröter, and S. G. Mishra (unpublished).

[4]R. J. Weiss, Proc. R. Soc. London **82**, 281 (1963).

[5]E. G. Moroni and T. Jarlborg, Physica B **161**, 115 (1989); Helv. Phys. Acta **62**, 195 (1989).

[6]P. Mohn, K. Schwarz, and D. Wagner, Physica B **161**, 153 (1989).

[7]O. K. Andersen, Phys. Rev. B **12**, 3060 (1975).

[8]O. Gunnarson and B. I. Lundqvist, Phys. Rev. B **13**, 4274 (1976).

[9]See, for instance, H. J. F. Jansen and S. S. Peng, Phys. Rev. B **37**, 2189 (1988); N. E. Christensen, O. Gunnarsson, and O. Jepsen, J. Phys. **49**, C8-17 (1988).

[10]V. L. Moruzzi, P. M. Marcus, K. Schwartz, and P. Mohn, Phys. Rev. B **34**, 1784 (1986).

[11]K. Hayashi and N. Mori, Solid State Commun. **38**, 1057 (1981); M. M. Abd-Elmeguid, B. Schleede, and H. Micklitz, J. Magn. Magn. Mater. **72**, 253 (1983).

[12]W. Bendick, H. H. Ettwig, F. Richter, and W. Pepperhof, Z. Metall. **68**, 103 (1977).

[13]G. Grimvall, in *Selected Topics In Solid State Physics,* edited by E. P. Wohlfarth (North-Holland, Amsterdam, 1986), Vol. XVIII; G. P. Renaud and S. G. Steinemann, Physica **149B**, 217 (1988).

[14]V. L. Moruzzi, J. F. Janak, and K. Schwarz, Phys. Rev. B **37**, 790 (1988).

[15]M. Matsui and S. Chikazumi, J. Phys. Soc. Jpn. **45**, 458 (1978).

[16]G. Haush and H. Warlimont, Acta Metall. **21**, 401 (1973).

[17]O. Yamada, F. Ono, I. Nakai, H. Maruyama, F. Arae, and K. Ohta, Solid State Commun. **42**, 473 (1982).

[18]M. Shiga and Y. Nakamura, J. Magn. Magn. Mater. **40**, 319 (1984).

[19]E. Kisker, E. F. Wassermann, and C. Carbone, Phys. Rev. Lett. **58**, 1784 (1987).

[20]M. Podgorny, J. Magn. Magn. Mater. **78**, 352 (1989).

[21]Y. Kakehashi, Phys. Rev. B **38**, 474 (1988); **38**, 12051 (1988).