PHYSICAL REVIEW B **70**, 012413 (2004)

Intersite elastic coupling and the Invar effect

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(Received 21 January 2004; revised manuscript received 16 April 2004; published 30 July 2004)

The Invar phenomenon (very small thermal expansion in some iron alloys or compounds) is usually explained by the thermally induced transitions between different spin states of Fe, having different atomic volumes. We consider these processes taking into account elastic interaction between Fe atoms in different spin states. Inclusion of these interactions explains why thermal expansion may be close to zero in a broad temperature interval and thus gives rise to the Invar effect.

DOI: 10.1103/PhysRevB.70.012413 PACS number(s): 75.50.Bb, 65.40.De, 75.20.Hr, 63.20.Ls

Invar behavior—the absence of the dependence of the lattice parameter on temperature in Fe-Ni alloys in certain concentration range, was discovered in 1897,[1] and similar behavior was found later in certain other systems, e.g., in ordered and disordered Fe_3 Pt and Fe_3 Pd.[2] The most plausible explanation of this phenomenon was suggested by Weiss,[3] who postulated the existence of two states of iron, close in energy: the ground state with the high spin, or the high-moment (HM) state with large specific volume, and the low-lying excited state with low spin or low moment (LM), having smaller atomic radius or specific volume. According to this picture, thermal excitation of the LM low-volume states causes lattice contraction, which counteracts and may cancel the usual positive thermal expansion. Although there is yet no definite proof of the existence of such two states in Invar alloys, many experimental facts are naturally explained in this picture.[2,4–6] The existence of almost degenerate states with different moments and different specific volumes is also corroborated by the detailed band-structure calculations.[7,8]

Recent neutron scattering studies[9] have confirmed the importance of magnetoelastic coupling for the Invar effect—apparently not the usual coupling present in magnetic materials with a given spin of the ions, but of the coupling with multiplet excitations, e.g., HM-LM excitation in iron. Although many particular details are still not clear, all these results confirm the general validity of the Weiss two-state model.

Of course the simple single-site picture proposed by Weiss, though very appealing, it is not sufficient for many purposes and has some issues to be resolved; see below. There are many attempts to go beyond of the model and to include intersite correlations. In most of these works (see, e.g., Refs. 7–9) *magnetic correlations between different sites* have been added. In the recent paper even noncollinear magnetic configurations have been proposed.[7] Although an experimental search for noncollinear configurations was not very successful,[10] they still might be important and can not be ruled out. In general, however, there is still no consensus as to the detailed nature of magnetic correlations and their role in the Invar effect.

In the present paper we want to explore the other physical factor—*elastic interactions between different sites*. These interactions, which are always present in real systems, can also modify the behaviour of the system and, as we will show, can "repair" some of the defects of a single-site two-state Weiss model.[3] Inclusion of these effects can significantly improve the description of Invar systems, even if we ignore intersite magnetic correlations, which, in general, could be also included.

The simple explanation of the Invar effect in the two-state model in the original form[3] is very transparent and appealing. However, one problem in this explanation becomes immediately apparent. The conventional thermal expansion is usually more or less linear in temperature

$$a(T) = a_0 + \alpha_0 T, \tag{1}$$

where $a(T)$ is the lattice parameter at a temperature T and α_0 is the conventional thermal expansion coefficient. On the other hand the thermal population of the low-spin state with smaller radius in simplest case of two well-defined LM and HM states would be exponential in temperature:

$$a(T) = a_0 - c \exp\left(-\frac{\Delta}{T}\right), \tag{2}$$

where $\Delta = E_L - E_H$ is the excitation energy of the LM state; $a_0 = a_H$; $c = (a_H - a_L)/2$; $a_{H/L}$ are the ionic radii of corresponding spin states. Thus, the question arises, how can one compensate in a reasonably broad temperature interval the normal positive thermal expansion (1), linear in T, by the extra negative contribution (2) which depends on the temperature *exponentially*.

The resolution of this problem should definitely lie in going beyond single-site description and taking into account coupling between different sites. Intersite magnetic correlations mentioned above are one possible mechanism. In this paper we suggest another simple mechanism that should always exist in real materials and that helps to resolve this paradox. When one discusses the coupling of the electronic excitations (here HM-LM excitation) to the lattice, this elastic interaction, besides coupling the electronic states with local deformation, usually leads also to an effective interaction *between different sites* (a somewhat similar interaction was also taken into account by Grüner *et al.*[11] in their Monte Carlo numerical simulations). One can easily show that if we consider predominantly a coupling to the short-range (or optical) vibrations, this intersite interaction will be essentially of antiferro type:[12–14] If we transform one site from a HM to a LM state with smaller volume, it would be favorable to have close to this small-volume LM ion the larger, i.e., HM ions. This interaction will modify the temperature dependence of the occupation of different spin states, and, consequently, will change the extra contribution to thermal expansion, effectively stretching the exponential temperature dependence (2). This would help to explain the almost full compensation of two mechanisms of thermal expansion—the usual one (1) and the additional stretched contribution, giving finally the Invar effect in a rather broad temperature interval.

One can describe this situation introducing the pseudospin operators, which describe two spin states, so that the state $\tau_i^z=+\frac{1}{2}$ corresponds to the HM state of an ion i and $\tau_i^z=-\frac{1}{2}$ to a LM state of it. The fact that these states have different ions radii (or atomic volumes) gives rise to a coupling of these states to the lattice, which classically can be written as:

$$H=-g\tau_i^z(v_i-v_0)+\frac{B}{2}(v_i-v_0)^2-\Delta\tau_i^z \tag{3}$$

Here v_0 is an average volume, $v_0=\frac{1}{2}(v_L+v_H)$, where v_L and v_H are the corresponding atomic volumes of the, respectively, LM and HM states, and $g=B(v_H-v_L)$ is the effective coupling constant. By minimizing the average energy $E=\langle H\rangle$ with respect to volume, we can indeed see that

$$v_i=v_0+\frac{g}{B}\tau_i^z, \tag{4}$$

which, with our choice of v_0 and g, reproduce the correct results, $v_i\left(\tau=\frac{1}{2}\right)=v_H$, $v_i\left(\tau=-\frac{1}{2}\right)=v_L$. We included in the Hamiltonian (3) also the term with the "magnetic field," $-\Delta\tau_i^z$, which describes the initial splitting of the HM and LM states: $\Delta=E_L-E_H$.

The model (3) describes only the single-site effects. But when one takes into account the coupling of local distortions around different sites (giving rise to the dispersion of phonons), one would get, besides these on-site effects, also an intersite interaction. If one rewrites the model (3) including the phonon dispersion,

$$H=\sum_{i,k}\tilde{g}_{ik}\tau_i^z(b_k^\dagger+b_k)+\sum_k\omega_k b_k^\dagger b_k-\Delta\sum_i\tau_i^z, \tag{5}$$

where $\tilde{g}_{ik}=\tilde{g}_k e^{ikR_i}$, one can in the usual way exclude the phonons by canonical transformation and obtain the effective pseudospin Hamiltonian, see, e.g., Ref. 13:

$$H_{\text{eff}}=\sum_{ij}\mathcal{J}_{ij}\tau_i^z\tau_j^z-\Delta\sum_i\tau_i^z,$$

$$\mathcal{J}_{ij}=-\sum_k e^{ik(R_i-R_j)}\frac{\tilde{g}_k^2}{\omega_k}. \tag{6}$$

The effective sign of an intersite interaction depends on the detailed k dependence of the spin-phonon matrix element $\tilde{g}_k$, on the phonon dispersion ω_k, and on the type of the lattice. One can easily show that the coupling via short-wavelength phonons leads to a nearest-neighbor repulsion $\mathcal{J}>1$, i.e. to an antiferromagnetic interaction between pseudospins τ, in accordance with the qualitative considerations presented above (the large HM state $\tau_1^z=+\frac{1}{2}$ would prefer to have nearby the low-volume LM sites, $\tau_j^z=-\frac{1}{2}$). Longer range interactions may in general have different sign,[14] but usually the nearest-neighbor (NN) interactions dominate, and this is what we will assume further on.

With this assumption we can reduce our model to an antiferromagnetic Ising model with NN coupling $\mathcal{J}$ in a parallel field. For Invar systems, the parameters of the model should be chosen such that the ground state corresponds to the HM state, i.e., all $\tau_1^z=+\frac{1}{2}$, which requires $\Delta>\mathcal{J}$. In this case the standard mean-field equation for the total (not the sublattice) magnetization takes the form:

$$\tau=\langle\tau\rangle=\frac{1}{2}\tanh\frac{\Delta-2\mathcal{J}z\tau}{2T} \tag{7}$$

(z is the number of nearest neighbors), from which we can determine the temperature dependence of τ and consequently, according to Eq. (4), of the average volume of our system,

$$v(T)=v_0+\frac{g}{B}\tau(T). \tag{8}$$

It is convenient to rewrite Eq. (7) as

$$\tau=\frac{1}{2}\tanh\frac{\tilde{\Delta}+2\mathcal{J}z\left(\frac{1}{2}-\tau\right)}{2T}, \tag{9}$$

where $\tilde{\Delta}=\Delta+2\mathcal{J}z\tau(0)=\Delta+\mathcal{J}z$ is the renormalized initial ($T=0$) splitting of the LM and HM states. If we would take this splitting to be constant [i.e., if we ignore the second term in the argument of Eq. (9)], we would get the conventional temperature dependence of τ (Brillouin function) and, consequently, of the lattice parameter and of the thermal expansion, which at low temperature would be exponential in temperature:

$$\tau(T)=\frac{1}{2}-\exp\left(-\frac{\tilde{\Delta}}{T}\right), \tag{10}$$

$$v(T)=v_H-\frac{(v_H-v_L)}{2}\exp\left(-\frac{\tilde{\Delta}}{T}\right),$$

cf. Eq. (2) [here $v(T=0)=v_H$]. This is what one would naively get in the standard Weiss model, which ignores the intersite interaction. As discussed above, we have then the problem, how this exponental contribution can compensate the usual linear positive thermal expansion in a broad temperature interval.

The analysis of Eq. (9) shows that when we include the intersite interaction $\mathcal{J}$, it leads, besides the renormalization of the initial splitting of LH and HM states, to the modification of the temperatures dependence of τ and, correspondingly, of the lattice parameters. This is shown in Fig. 1, in which we present the results of the calculations for representative values of parameters $\Delta=550$ K, $\mathcal{J}z=440$ K. The dotted line is the dependence of $\tau(T)$ [or of an extra contribu-

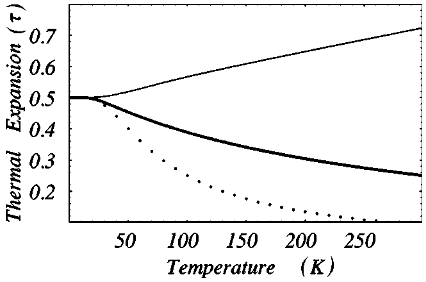

FIG. 1. The extra negative thermal expansion [see Eq. (9)] without intersite elastic interaction (dotted line) and with this interaction taken into account (solid line). The thin line is a conventional positive thermal expansion.

tion to the volume $v(T)$] ignoring the intersite elastic interaction [the term with $\mathcal{J}$ in Eq. (9)], and the solid line represents this interaction taken into account. By the thin line we qualitatively show the conventional positive thermal expansion which behaves as $\sim T^4$ at low temperatures and goes over to linear dependence for higher T. We see indeed that, whereas without intersite interaction ($\mathcal{J}=0$), (see the dotted line in the figure) τ changes with temperatures rather steeply [initially as $\frac{1}{2}-\exp(-\tilde{\Delta}/T)$], with nonzero intersite coupling $\mathcal{J}$ this dependence becomes much smoother (see the solid line in the figure). This is easy to understand: if indeed there exists a repulsion between similar spin states [antiferromagnetic coupling in Eq. (6)], then the thermal excitations of certain amount of LM states hinder corresponding transitions on neighboring sites, so that as a result the average excitation energy $\tilde{\Delta}+\mathcal{J}z\left[\frac{1}{2}-\tau(T)\right]$ would gradually increase with temperature, making the extra negative contribution to lattice parameter more smooth. If we now add to this term the usual positive thermal expansion (qualitatively shown in Fig. 1 by thin line), we indeed see that with $\mathcal{J}\neq 0$ one can get a better cancellation of the normal and anomalous contributions to thermal expansion (although this cancellation is not exact).

This is the main conclusion of the present paper. We used the fact that the elastic interaction between different spin (and volume) states of Fe in Invar alloys is always present. We have shown that the inclusion of the elastic interactions helps to resolve some of the problems inherent to the two-state (Weiss) model traditionally used in this field. The essence of our results is that due to this elastic interactions between HM and LM states of Fe ions the effective energy separating low moment/small volume and high moment/large volume states in Invar alloys becomes temperature and concentration dependent. This modifies the temperature dependence of the thermal expansion and finally guarantees the Invar behavior in a broad temperature interval.

We have to stress that one should not take the notions of HM and LM states of Fe ions too literally, in the same way as we treat high spin (HS) and low spin (LS) states of Fe^{2+} in insulators. There indeed the ionic radii of corresponding states differ a lot. In contrast, we are dealing here with metallic systems, in which it is not even clear whether we can assign a particular valence (e.g., 2+) to Fe sites. Therefore, retaining partially the "genetic" connection with the HS and LS states of well defined Fe^{2+} ions, corresponding states in Invar alloys may have much smaller difference in specific volumes, as observed by Robertson *et al.*[6] In our opinion it is an unavoidable consequence of metallic character of corresponding systems (that is why, by the way, we choose to use the notation HM/LM instead of the conventional HS/LS states). But, despite that, the physical mechanism invoked in our paper—elastic intersite interactions, or, more accurately, *spin state–phonon interactions*, should be present also in this case, and, as we have found in the framework of our simple model, may strongly contribute to the Invar phenomenon.

It is also important to note that most of Invar systems are alloys, mainly disordered (although some of them, such as Fe$_3$Pt, are ordered, i.e., are rather intermetallic compounds). The main role of the second component of the alloys is apparently to control the effective splitting between HM and LM energy levels, so that, e.g., for too low concentration of Ni in Fe-Ni alloys the excitation energy may be too large to lead to noticeable effects in an interesting temperature interval, and in the opposite limit the LM/small volume state may become the ground state, in which case we will get only the extra contribution *increasing* positive thermal expansion. Disorder of course may play some role but just the original Weiss model is in a sense less sensitive to it than many later refined versions. Our treatment based on the introduction of elastic coupling between Fe sites does not need a regular, ordered state, and does not require all neighbors of a given Fe being also Fe. Each time Fe ions are neigbors, our mechanism would work; the only difference would be that instead of the number of nearest neighbors z in our Eqs. (7) and (9) there will be an average number of neighboring Fe's, which for random alloys of the type Fe$_x$Ni$_{(1-x)}$ would be in average equal to zx. As we do not aim at quantitative results and use $\mathcal{J}z$ as a free parameter, the substitution of $\mathcal{J}z$ by $\mathcal{J}zx$ would not change our qualitative conclusions. Another consequence of the random distribution of the "active" (Fe) and "passive" (Ni) components may be certain broadening of the distribution of these level splittings, which will also smooth out the temperature dependence of the properties of Invar alloys.

Extra consequences of our treatment are, first, that due to this effect the energy separation of these two states becomes dependent on the local coordination (occupation of neighboring sites); this can hinder the direct observation of these two-level-systems, e.g., by the neutron scattering. On the other hand, there should appear certain correlation in the occupation of different magnetic states; this effect should be observable experimentally. This could even lead to the formation of some textures in the Invar samples.

Some of the factors important for the Invar phenomenon, such as the role of magnetic correlations and the metallic nature of most of the Invar systems, were not included in our treatment. Nevertheless, even in this simplified form the model considered above, with the inclusion of the intersite elastic interactions, can explain the main features of the Invar systems, and these interactions definitely have to be taken into account in the full theory of the Invar effect.

We are grateful to M. Abd-Elmeguid, K. Neumann and K.R.A. Ziebeck for useful discussions. This work was supported by the German Physical Society via SFB 608 and by the Leverhulme Trust.

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