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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.

Invar behaviour – 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 behaviour 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 experimented facts are naturally explained in this picture [2,4,5]. The existence of almost degenerate states with different moments and different specific volumes is also corroborated by the detailed band-structure calculations [6,7].

Recent neutron scattering studies [8] 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 mutliplet excitations, e.g. $HM-LM$ excitations iron. Although many particular details are still not clear, all these results confirm the general validity of the Weiss two-state model.

This simple explanation of the invar effect is very 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:

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

where $\triangle = E_L - E_H$ is the excitation energy of the LM state, and $a_0 = a_H$; $c = (a_H - a_L)/2$; $a_{H/L}$ 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*.

In this paper we suggest the simple mechanism which should always exist in real materials and which helps to resolve this paradox. When one discusses the coupling of the electronic excitations (here HM - LM excitation) to the lattice, this interaction, besides coupling the electronic static with local deformation, usually leads also to an effective interaction *between different sites* (somewhat similar interaction was also taken into account by Grüner et al. [9] 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 [10]: If we

transform one site from a HM to a LM state with smaller volume, it would be favourable 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:

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

Here v_0 is an average volume, $v_0 = \frac{1}{2}\big(v_L + v_H\big)$, where v_L and v_H are the corresponding atomic volumes of the respectively LM and HM states, and $g = B\big(v_H - v_L\big)$ is the effective coupling constant. By minimizing the average energy $E =< H >$ 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, $v_i\big(\tau = \frac{1}{2}\big) = v_H$, $\;v_i\big(\tau = -\frac{1}{2}\big) = v_L$. 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: $\triangle = E_L - E_H$.

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 phonons dispersion,

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

where $\tilde{g}_{ik} = \tilde{g}_k e^{ikRi}$, one can in the usual way exclude the phonons by canonical transformation and obtain the effective pseudospin Hamiltonian, see e.g. [11]:

$$H_{eff} = \sum_{ij}\mathcal{J}_{ij}\tau_i^z\tau_j^z - \Delta\sum_i\tau_i^z \tag{6}$$

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

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 [12], but usually the 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 sublattice!) magnetization takes the form:

$$\tau =< \tau >= \frac{1}{2}\ th\frac{\Delta - 2\mathcal{J}z\tau}{2T} \tag{7}$$

(z is the number of nearest neighbours), from which we can determine the temperature dependence of τ and consequently, according to (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

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

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. (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 equation (9) shows that when we include the intersite interaction, it leads, besides the renormalisation 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 contribution to the volume $v(T)$) ignoring the intersite elastic inteaction (the term with $\mathcal{J}$ in equation (9)), and the solid line – with this interaction taken into account . By 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 ($\mathcal{J} = 0$), τ changes with temperatures rather steeply (initially as $\frac{1}{2} - \exp\left(-\frac{\tilde{\Delta}}{T}\right)$), with non-zero intersite coupling $\mathcal{J}$ this dependence becomes much smoother.This is easy to understand: if indeed there exists a repulsion between similar spin states (antiferromagnetic coupling in equation (6)), then the thermal excitations of certain amount of LM states hinder corresponding transitions on neighbouring 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).

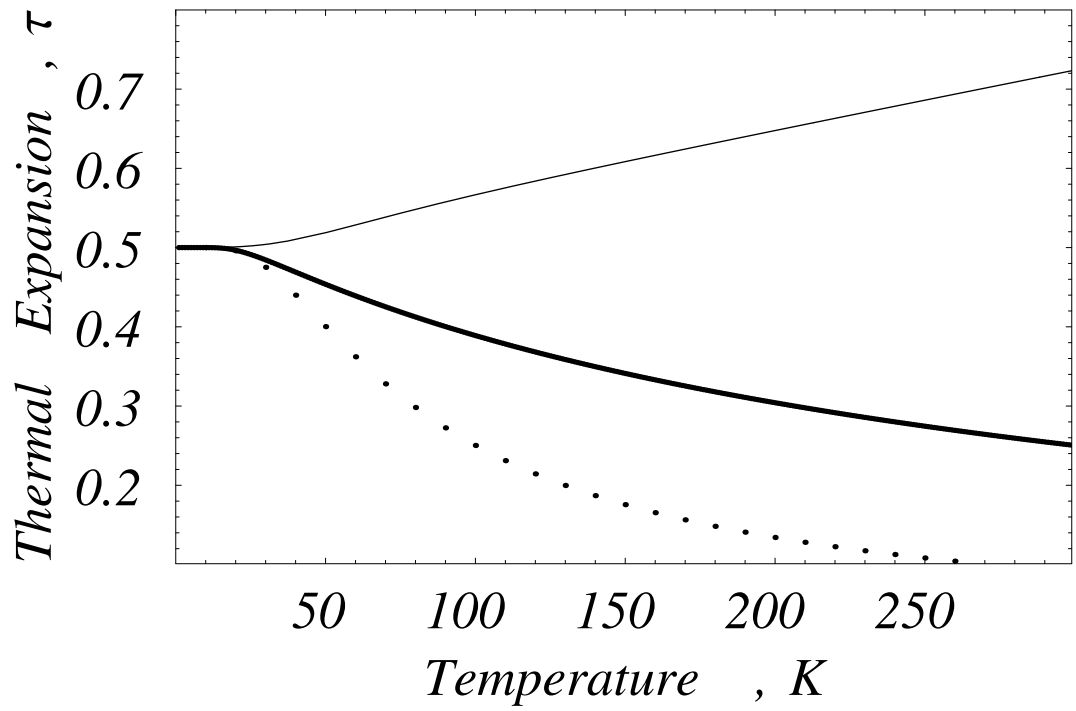

Fig.1 The extra negative thermal expansion(see Eq.(9)) without intersite elastic interaction (dotted line) and with this interaction taken into account (solid line). Thin line is a conventional positive thermal expansion.

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 show that its inclusion 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 interaction the effective energy separating low moment/small volume and high moment/large volume states in invar alloys becomes temperature-dependent. This modifies the temperature dependence of the thermal expansion and finally guarantees the invar behaviour in a broad temperature interval.

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 neighbouring 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.

Many of the problems in this field still remain open. One of them is the role of magnetic ordering for the invar phenomenon, which was not included in the present treatment. Another problem is the account of the metallic nature of most of the invar systems. 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.

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