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The forbidden phonon mode in Fe–Ni Invar

S Lipiński†, K-U Neumann‡ and K R A Ziebeck‡

† Institute of Molecular Physics, Polish Academy of Sciences, Smoluchowskiego 17, 60-179 Poznań, Poland

‡ Department of Physics, Loughborough University of Technology, Loughborough, Leicestershire LE11 3TU, UK

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Abstract. A simple analysis of the breaking of the symmetry of the phonon modes by slow distortions is presented. A phenomenological model is put forward for an explanation of the recently discovered 'forbidden mode' in $Fe_{65}Ni_{35}$ Invar alloy.

1. Introduction

Invar alloys are characterized by an invariant thermal expansion up to room temperature, a feature that renders Invars to be of great technological importance. The most widely discussed system of this family is the FCC $Fe_{65}Ni_{35}$ alloy. For a recent review we refer to [1]. The simultaneous occurrence of unusual magnetic and elastic properties suggests that a coupling of the magnetization to the lattice is essential for the Invar effect [2]. Only a few of the Invar anomalies will be mentioned here. All three elastic constants, the longitudinal C_L and the shear elastic constants C_{44} and C', show a pronounced softening over the temperature range for which the thermal expansion coefficient is practically zero. The spin-wave spectra can only account for approximately half of the decrease of the magnetization with increasing temperature. Furthermore, the spin-wave linewidths are found to be much larger than for other ordinary ferromagnets not exhibiting Invar behaviour.

Recent fixed-spin-moment spin-polarized total-energy band calculations for Invar [3, 4] indicate the coexistence of almost degenerate states characterized by different magnetic moments and also different volumes. Low-spin (LS) solutions are found for low volume and high-spin (HS) at high volumes. The concept of the coexistence of HS and LS states proved to be successful in explaining the absence of significant thermal expansion [5]. The nature of the mixing of HS and LS states remains unclear [5]. Some authors suggest the existence of more than two competing states. KKR CPA calculations [6, 7] predict a crossover in the Invar region from the HS state to a state of magnetic disorder and then to a non-magnetic state. Experimentally the notion of an HS–LS state transition is supported by an investigation of the temperature dependence of the photoemission intensity of ordered Fe_3Pt [8] and by measurements of the pressure dependence of Mössbauer spectra in $Fe_{68}Ni_{32}$ and in ordered and disordered $Fe_{72}Pt_{28}$ [9, 10]. A number of Invar models that do not use the concept of HS and LS states have been put forward. For example within the weak-ferromagnet approach [11, 12] it is assumed that the Invar effect is a consequence of a gradual transition from strong to weak magnetism due to thermal excitations. Many authors stress the importance of metallurgical and magnetic inhomogeneity [13, 14], since the magnetovolume effects reach a maximum within a concentration within which the γ–α transition occurs.

The inhomogeneous models as well as theories of weak ferromagnetism are relevant for Fe–Ni Invar, but the fact that Invar effects occur also in ordered, strong ferromagnets (e.g. Fe_3Pt) suggests that other mechanisms are of importance. In order to understand the discrepancy between the spin-wave stiffness constant D_{sw} (as determined by neutron scattering) and D_m (as determined from the temperature dependence of the magnetization ($T^{3/2}$ law)) Ishikawa and co-workers [15] introduced the concept of 'hidden excitations'. They proposed that hidden excitations are only seen on a long time scale (i.e. they contribute to the magnetization) and are not sensed by neutrons. At present Ishikawa's assumption of hidden excitations is a point of lively and controversial discussion. It is argued that this concept was introduced by a poor analysis of experimental data and that the expression of the magnetization taking properly into account the magnon linewidth and the Bose factor can resolve the discrepancy between D_m and D_{sw}. A similar problem has been discussed in the papers on inhomogeneous magnetic systems (surfaces, [16]; modulated structures [17]), where it was pointed out that in order to reproduce the temperature dependence of the magnetization it is no longer sufficient to know just the curvature at the bottom of the spin-wave band but instead a precise knowledge of the whole spin-wave spectrum is required. Despite this criticism the 'hidden-excitations' concept is widely used as a working hypothesis. In their recent paper on Fe–Ni films [18] Wassermann *et al* suggest that these excitations are of structural origin, and they propose [1] that the volume-coupled HS–LS transitions give rise to such excitations. Very recently a structural instability in FCC ordered Fe_3Ni alloy with respect to small tetragonal or shear deformations was put forward [19]. Fe_3Ni is close in concentration to the Invar composition. Our TB LMTO CPA calculations for disordered $Fe_{65}Ni_{35}$ [20] also show that in Invar not only magnetovolume (η_0) but also *magnetodistortive instabilities exist, which have tetragonal* (η_1) *or orthorhombic* (η_3, η_4, η_5) symmetry.

$$\begin{aligned} &\eta_0 = \eta_{11} + \eta_{22} + \eta_{33} \qquad \eta_1 = (2\eta_{33} - \eta_{22} - \eta_{11})/\sqrt{3} \\ &\eta_3 = \eta_{23} \qquad \eta_4 = \eta_{13} \qquad \eta_5 = \eta_{12} \end{aligned} \tag{1}$$

where η_{ij} are the Lagrangian strain-tensor components for the cubic $m3m$ Laue group [21].

In general the distortions $a\eta_0 + b\eta_1$ are energetically more favourable than those with no volume change (η_i) [20]. It is not surprising that tetragonal and orthorhombic distortions induce a magnetic instability, since, similar to the totally symmetric distortion (volume change), they are effectively changing the nearest-neighbour (NN) distance. The magnetic instability in Invar is a consequence of the particular position of the Fermi level. The Fermi level is located just above the majority t_{2g} peak and in between the t_{2g} and e_g minority peaks [4, 6, 7, 22, 23]. A decrease of the NN distance broadens the t_{2g} minority subband and a repopulation between the minority t_{2g} and e_g subbands results. For a critical value of the NN distance the change in occupation of the t_{2g} minority orbitals is large enough to shift the majority atomic levels with t_{2g} character (via the Coulomb interaction with the minority electrons) and to move the t_{2g} majority peak from its position just below E_F to partly above. Because of the large number of states for both spin directions around E_F this shift corresponds to a rapid drop of the magnetic moment. It is believed that the magnetodistortive fluctuations mentioned above also play the role of Ishikawa's 'hidden excitations'. It will be shown below that a magnetic instability is essential for an understanding of the recently discovered 'forbidden' phonon acoustic mode [24]. Inelastic-neutron-scattering experiments undertaken on a single crystal of Ni–Fe at the Invar composition revealed the presence of a transverse phonon mode in scans for which its cross-section should have been zero. Extensive measurements were made in the principal symmetry directions but the effect was only observed for momentum transfer along the [001] direction. The measurements were repeated under different experimental conditions e.g. by changing the crystal orientation or final wave vector and the 'forbidden' mode was observed in all experiments. However, measurements carried out under identical experimental conditions on an Ni crystal and two Ni–Fe crystals of different composition away from the Invar region failed to reveal the 'forbidden' transverse mode. It was concluded that the appearance of the mode was intrinsic to the Invar composition. The experiments were carried out using neutron polarization analysis, which enabled the polarization ratios of the modes to be measured and hence the dynamic form factor to be determined.

The present paper is the first attempt at understanding this interesting forbidden-mode phenomenon. In the next section a phenomenological Landau–Ginzburg model is introduced that contains the essential features of the phenomenon—the coupling of the lattice with the magnetic system close to the magnetic instability.

2. Model

We consider the FCC system close to the magnetodistortive instability and write the total energy as a sum of a magnetic, a lattice and a magnetoelastic contribution. For simplicity we use the NN approximation.

$$E = E_{\mathrm{m}} + E_{\mathrm{L}} + E_{\mathrm{m-L}} \tag{2}$$

where

$$E_{\mathrm{m}} = \sum_i A_i M_i^2 + \sum_i B M_i^4 + \sum_i C M_i^6 + \sum_{ij} D M_i M_j \tag{3a}$$

$$E_{\mathrm{L}} = \sum_{i\alpha} \frac{p_{i\alpha}^2}{2m} + \sum_{ij\alpha} K_1^{\alpha}(i-j)(\zeta_i^{\alpha} - \zeta_j^{\alpha}) + \sum_{ij\alpha\beta} K_2^{\alpha\beta}(i-j)(\zeta_i^{\alpha} - \zeta_j^{\alpha})(\zeta_i^{\beta} - \zeta_j^{\beta}) \tag{3b}$$

$$E_{\mathrm{m-L}} = \sum_{ij\alpha} D_1^{\alpha}(i-j)(\zeta_i^{\alpha} - \zeta_j^{\alpha}) M_i M_j + \sum_{ij\alpha\beta} D_2^{\alpha\beta}(i-j)(\zeta_i^{\alpha} - \zeta_j^{\alpha})(\zeta_i^{\beta} - \zeta_j^{\beta}) M_i M_j. \tag{3c}$$

It is assumed that the magnetic instability can be reached by a decrease of the NN distance. It is pointed out that this does not necessitate the uniform and isotropic decrease in the NN distance. The coefficients are chosen such that $B < 0$, $C > 0$ and

$$A_i = \alpha\left(\sum_n \Delta_n \Theta(\Delta_n) - \Delta_{\mathrm{c}}\right) \qquad \alpha > 0 \qquad \Delta_{\mathrm{c}} > 0. \tag{4}$$

Here n runs over NN only.

$$\Delta_n = -\boldsymbol{\delta}_n \cdot \boldsymbol{T}(n). \tag{5}$$

$\boldsymbol{\delta}_n$ and $\boldsymbol{T}(n)$ denote the NN position vector and displacement respectively and Θ is a step function.

The microscopic source of the instability (4), as was mentioned earlier, is a contraction of the t_{2g} bonds.

ζ_i^α is in general a resultant of two terms: a static local distortion and a dynamic one

$$\zeta_1^\alpha(t) = s_1^\alpha + u_1^\alpha(t). \tag{6}$$

Substituting (6) into (3) one obtains

$$\begin{aligned} E_L + E_{m-L} = {} & \sum_{ij\alpha}(K_1^\alpha(i-j) + D_1^\alpha(i-j)M_iM_j)(s_i^\alpha - s_j^\alpha) \\ & + \sum_{ij\alpha\beta}(K_2^{\alpha\beta}(i-j) + D_2^{\alpha\beta}(i-j)M_iM_j)(s_i^\alpha - s_j^\alpha)(s_i^\beta - s_j^\beta) \\ & + \sum_{ij\alpha}[K_1^\alpha(i-j) + D_1^\alpha(i-j)M_iM_j \\ & + 2\sum_\beta(K_2^{\alpha\beta}(i-j)(s_i^\beta - s_j^\beta) + D_2^{\alpha\beta}(i-j)(s_i^\beta - s_j^\beta)M_iM_j)](u_i^\alpha - u_j^\alpha) \\ & + \sum_{i\alpha}\frac{p_{i\alpha}^2}{2m} + \sum_{ij\alpha\beta}(K_2^{\alpha\beta}(i-j) + D_2^{\alpha\beta}(i-j)M_iM_j)(u_i^\alpha - u_j^\alpha)(u_i^\beta - u_j^\beta). \end{aligned} \tag{7}$$

It is not intended here to discuss the energetics of the possible distortions represented by the first two terms in (7). Furthermore we are not interested here in phonon relaxation with the mechanism given by the third term. The parameters used in the model are assumed to be such that the distortions specified by

$$\sum_n \Delta_n \Theta(n) \geqslant \Delta_c \tag{8}$$

are thermally accessible and we only want to examine the consequences of the model assumption on the dynamics of the lattice. The microscopic justification of the above assumption, particularly for Invar, is given by the small energy differences between the LS and HS states with different volumes and for a tetragonal or an orthorhombic distortion. For Fe–Ni Invar the energy differences are of the order of 0.5 mRyd/atom [20]. To be precise, instead of using HS, LS states in the oversimplified picture (3, 4) we shall use FM ($M = M_0$) and NM ($M = 0$) states. On the phonon time scale we can treat the volume and distortive fluctuations as static and they are assumed to be randomly distributed.

3. Breaking of the lattice mode symmetry

In the following we are only interested in a qualitative understanding of the possible breaking of the lattice mode symmetry. Local distortions influence the dynamical matrix indirectly via the possibility of destroying the local magnetization on a given site i (A_i at this site changes from negative to positive in (4)). The perturbation introduced thereby can be written as

$$R^{\alpha\beta}(i,j) = D_2^{\alpha\beta}(i-j)(M_iM_j - M_0^2). \tag{9}$$

It should be mentioned that expanding the energy (6) beyond second order in displacements, in addition to the magnetic terms also non-magnetic perturbations of the dynamical matrix will arise. The latter effect results from the local change of the geometrical symmetry introduced by the distortion. However due to the harmonic approximation used above (3, 7) this is outside the scope of the present paper.

Since the quasistatic 'distortion clusters' (local distortions) are assumed to be randomly distributed the perturbation (9) does not mix the modes with different wave vectors. For a given set of N identical non-overlapping clusters one obtains the Fourier transform of (9) in the form

$$R^{\alpha\beta}(q) \equiv R^{\alpha\beta}(q, q') = \delta_{qq'} c \sum_{ij} D_2^{\alpha\beta}(i-j)(M_i M_j - M_0^2) \mathrm{e}^{\mathrm{i}q(i-j)} \tag{10}$$

where i, j run within the cluster and in the NN shell and c is the distortion cluster concentration. A generalization of (10) that takes into account a possible distribution of clusters is straightforward and we do not discuss it here. In the oversimplified model proposed here the possibility of chemical inhomogeneities is not taken into account. Their role will be briefly commented on later. The following discussion will concentrate on the phonon modes in two high-symmetry directions that have been examined experimentally [24], namely [100] and [110]. For cubic systems these modes are constrained by symmetry to be purely transverse or purely longitudinal. One can expect longitudinal–transverse mode mixing for [100] if $R^{xy}(q) \neq 0$ and for [110] if $R^{yy}(q) \neq R^{xx}(q)$. For both directions the only contribution to the matrix elements of interest (R^{xy}, R^{xx}) arises solely from the NNs within the xy plane. For the [100] direction this occurs because $D^{xy}(i-j)$ vanishes if i and j are not located in the same xy plane and for [110] because this direction is perpendicular to all the NN vectors outside the xy plane. This remark significantly simplifies the picture since one can now investigate separately the contributions arising from distinct xy planes. Thus any distortion that preserves all the cubic symmetry operations within the xy plane does not mix the cubic symmetry modes of wavevectors from the plane $q_x q_y$. Neither the totally symmetric distortion η_0 nor the tetragonal one η_1 break this symmetry. However the orthorhombic distortion does break the symmetry. The last point may be illustrated by reference to the simplest non-trivial example shown in figure 1(a)—the NN orthorhombic distortion $T_5 = \Delta\eta_{12}\delta(r - \sqrt{2}/2)$. In figure 1($b$) the corresponding magnetic and harmonic force perturbations are shown for $2\sqrt{2}\Delta \geqslant \Delta_c$. The distortion of the lattice is not shown in figure 1(b) since as mentioned earlier there is no direct effect on the dynamical matrix by the change in the lattice-site position if one is restricted to the harmonic approximation. The perturbation of the dynamical matrix elements $R^{xy}(i-j)$ are given below:

$$\begin{aligned} &R^{xy}(\tfrac{1}{2}, \tfrac{1}{2}, 0) = R^{xy}(-\tfrac{1}{2}, -\tfrac{1}{2}, 0) = -\gamma M_0^2 \\ &R^{xy}(\tfrac{1}{2}, -\tfrac{1}{2}, 0) = R^{xy}(-\tfrac{1}{2}, \tfrac{1}{2}, 0) = \gamma M_0^2 \\ &\gamma = D_2^{xy}(\tfrac{1}{2}, \tfrac{1}{2}, 0). \end{aligned} \tag{11}$$

Each bond (the broken lines in figure 1(b)) contributes a value $(\pm 2\gamma/N) M_0^2 \cos(\tfrac{1}{2}q)$ to the transform $R^{xy}(q, 0, 0)$ but the terms inside the cluster cancel. This reflects the fact that inside the cluster the symmetry of the perturbed force constants is still cubic. It is broken for the NN shell (full points), yielding

$$R^{xy}(q, 0, 0) = (-4\gamma/N) M_0^2 \cos(\tfrac{1}{2}q). \tag{12}$$

That this matrix element does not vanish implies that for the [100] direction the modes do not preserve their purely longitudinal or transverse character, as was discovered in Invar by neutron scattering [24]. It is worth mentioning that whereas the mixing weight of the modes is determined by R^{xy} alone the eigenvalues are also influenced by a number of other perturbations, some of which preserve cubic symmetry. In a similar way as above it is easy to check that for the [110] direction

$$R^{xx}(q,q,0) = R^{yy}(q,q,0) = (-12/N)D_2^{xx}(\tfrac{1}{2},\tfrac{1}{2},0)M_0^2\cos(q). \tag{13}$$

The equality of the matrix elements (13) is a consequence of the orthorhombic symmetry of the perturbed system with x' and y' as the symmetry axes (figure 1(*a*)). It may be concluded that for the [110] direction no mixing of the modes occurs, which is in agreement with experimental observation [24].

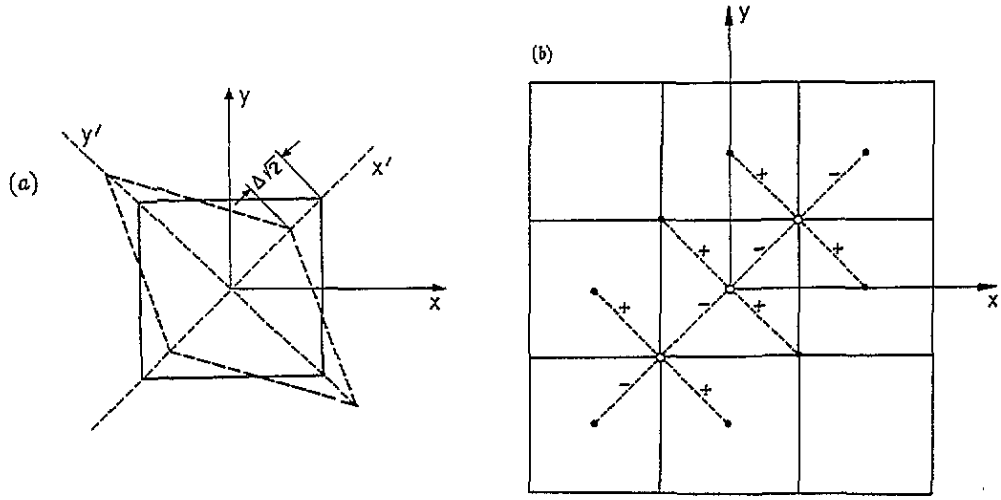

Figure 1. (*a*) The orthorhombic distortion $T_5 = \Delta\eta_{12}\delta(r - \sqrt{2}/2)$. (*b*) The induced magnetic and harmonic force perturbations for $2\sqrt{2}\Delta \geqslant \Delta_c$. The open circles denote the sites where the magnetic moment has collapsed. The broken lines with the marked signs represent $R^{xy}(i-j)$.

To summarize, it has been the aim to obtain an explanation for the observation of the forbidden mode in Invar with an argument based solely on symmetry. The present model (although it mimics the essential magnetodistortive instability and its influence via the harmonic magnetoelastic coupling on the symmetry of the phonon modes) omits all the richness of the magnetodistortive phenomena in Invar. This concerns the magnetic distribution and space extensions of the distortive fluctuations, which are important for the quantitative calculations but were omitted in the qualitative picture presented above. Here we have only shown that among the distortions that do not cost much energy a special role is played by the local orthorhombic distortions in giving rise to the forbidden mode. Due to the magnetoelastic coupling, they locally break the cubic symmetry of the dynamical matrix and thus act on the [100] phonon mode as the local polarizer. Due to the long time scale of the independent distortion fluctuations they are seen by phonons as a set of randomly frozen perturbations. In general modes with different wavevectors do not mix. Similar phenomena can be expected in other systems where the distortions can induce magnetic instabilities. Very recently the 'forbidden modes' have been observed in Tb–Zn [25].

The present paper has been devoted to a discussion of the distortion mechanism of the occurrence of the forbidden phonon mode. The early local models of Invars [13, 14, 26] based on Mössbauer experiments [26] stress that the chemical inhomogeneity is important for inducing the magnetization inhomogeneity. One has to consider the chemical clusters as a complementary source for the perturbation of the dynamical matrix. Neutron-scattering experiments [27] reveal that clusters are either highly elongated or flattened rather than spherical, a fact that makes them relevant for the present problem of local symmetry breaking. Experimentally a substantial intensity is observed for the forbidden mode at 5 K [24]. Due to the Boltzmann factor the distortion-induced perturbation is temperature dependent with the energy scale being determined by the energy of the distortion fluctuations. The intensity increases by one half for 100 K [26]. The compositional inhomogeneities are expected to also influence the spread of distortion energies. Taking into account the chemical inhomogeneities the spread of the energy difference between HS and LS states, as determined by band-structure calculations, will be modified [20]. For an Fe concentration of $x = 0.68$ ($x = 0.65$) this energy difference takes a value of 0.15 mRyd/atom (0.47 mRyd/atom), which suggests that even at low temperatures the role of the distortion perturbation may not be negligible. Effects of chemical environments will be studied in detail in a forthcoming paper.

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