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Magnetoelastic coupling model for fluctuating-valence $\text{Ce}(\text{Ni}_{1-x}\text{Co}_x)\text{Sn}$ ($0.35 \leq x \leq 0.40$) compounds at high magnetic fields and temperatures

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Abstract. A model of magnetoelastic coupling has been developed which explains the volume and anisotropic magnetostriction thermal dependences of the fluctuating-valence intermetallic compounds $\text{Ce}(\text{Ni}_{1-x}\text{Co}_x)\text{Sn}$, above their valence transition temperatures and in a strong magnetic field (14 T), in the range $0.35 \leq x \leq 0.40$. The model assumes narrow 4f-conduction electron hybridized bands, where only the ground-state $|\pm 3/2\rangle$ bands are populated, and that the magnetoelastic coupling stems from the interaction of the Ce^{3+} ion with the site crystal electric field. As a result the values of the corresponding microscopic magnetoelastic coupling parameters of volume ($M^{\alpha,1}$) and tetragonal ($M^{\alpha,2}$) characters have been determined for $x = 0.38$. Their values (about 10–50 K/ Ce^{3+}) are unusually *large* for unstable 4f-shell intermetallics.

1. Introduction

Magnetostriction is a phenomenon which needs some preliminary considerations, mainly because we are dealing with 4f fluctuating-valence (FV) systems. For itinerant or band electrons we have to deal with their localized or quasi-localized character. That is because the only coupling between the isotropic spin magnetism and the atomic orbital structure is spin-orbit coupling, which induces a non-zero average orbital magnetic moment. This moment in 3d transition metals is, however, very weak. Magnetic anisotropy and magnetostriction arise from the interaction of the electronic orbital momentum with the site crystal electric field (CEF). It is noticeable that the contribution to the magnetic anisotropy and magnetostriction is due, mainly, to high-symmetry points of the Brillouin zone (BZ), where orbital states are not mixed by interband hopping and their orbital momentum is almost a constant of motion [1].

On the contrary, in well localized 4f states their coupling to the lattice CEF is rather weak, if compared to spin-orbit coupling. Magnetic anisotropy and anisotropic magnetostriction again arise from the interaction of the rather well defined ionic orbital states with the site CEF. However, if these localized states become hybridized with the conduction band electrons, the nature of this hybridization strongly influences their interaction with the local environment. In this way the band or quasi-band character of the hybridized 4f electrons can be essential to their magnetoelastic behaviour, which is the situation for FV systems. This hybridization does not allow us to consider the local states in FV systems

as infinitely narrow. In fact, one has to consider maxima of the density of electronic states with given widths. These widths and the energy centres of these maxima, measured for example with respect to the Fermi level μ , determine the existence of local magnetic moments [2]. Therefore their magnetoelastic behaviour should depend on the detailed nature of these quasi-local states. Then we must consider, in principle, that the anisotropic and volume magnetostrictions in FV systems should depend on field, temperature and pressure in quite a complex way.

In the present work we have dealt with the series of pseudo-ternary intermetallic compounds $\text{Ce}(\text{Ni}_{1-x}\text{Co}_x)\text{Sn}$. A thorough description of their structural, transport, magnetic and magnetoelastic properties together with the observed magnetic excitations can be found elsewhere [3,4]. Here we shall summarize only those experimental aspects which are relevant to our work. The present series crystallizes in the orthorhombic TiNiSn structure with $Pnma$ space group, the Co–Ni being probably substitutionally disordered [5]. CeNiSn is a small-gap (about 4 K) Kondo insulator [4,6], the gap at the Fermi level decreasing with Co addition and finally disappearing for $x = 0.25$, according to electrical resistivity measurements [4,7]. The temperature dependence of the low-field susceptibility χ shows a dramatic change with Co concentration [4,7]; for $0 \leq x \leq 0.34$, $\chi(T)$ has a form which shows an increasing trend towards FV behaviour with increasing x : for $x = 0.34$, $\chi(T)$ exhibits a broad maximum at 95 K; for $0.35 \leq x \leq 0.40$, $\chi(T)$ exhibits a sharp drop at temperatures between 40 and 75 K (dependent on x). Therefore for the Co content range $0.35 \leq x \leq 0.40$ the system depicts, at temperatures $T_v \simeq 40\text{--}75$ K, a first-order valence transition, towards an electronic average configuration $4f^{1-\delta}$. A giant contraction ($\Delta\omega_s \approx 0.3\%$ for $x = 0.38$) in the spontaneous volume magnetostriction ω_s measured by both neutron diffraction and thermal expansion is observed at T_v [3,4]. For the above range of x , the unit cell is pseudo-tetragonal, i.e. the lattice parameters $a \simeq b$ [4]. (Note that we have arbitrarily called a and b the almost similar lattice parameters and c , the unequal lattice parameter, as customarily done for tetragonal symmetry.) Inelastic neutron scattering (INS) measurements [4] performed above T_v on the $x = 0.38$ compound give a quasi-elastic line, together with two crystal-field excitations at 26.5 meV and 42.1 meV. Magnetostriction measurements performed at an applied magnetic field of 14 T on polycrystalline samples show a large volume magnetostriction ω and a large anisotropic magnetostriction λ_t , for the above x range, with first-order jumps at T_v and a strong decrease just below T_v [3].

Still, we would like to look for an experimental situation where the above-mentioned limitations for a theoretical description could be relaxed, at least within a given range of external parameters, e.g. temperature. However, the nature of the temperature-induced phase transition from the high-valence state to the FV state observed in the $\text{Ce}(\text{Ni}_{1-x}\text{Co}_x)\text{Sn}$ system [3,4,7] is complicated by the fact that it is probably a many-body effect, which could be properly explained either within the Anderson-lattice Hamiltonian [8] or within the tight-binding Hubbard framework [9]. In this work we are interested in the temperature dependences of the field-induced irreducible strains of the following [10]: volume strain $\epsilon^{\alpha,1}$ and tetragonal strain $\epsilon^{\alpha,2}$. The temperature range that we are interested in is only above T_v and we shall focus on the $x = 0.38$ compound, where ω and λ_t are the largest measured magnetostrictions among the present series, and where we deal with the INS linewidths needed for our calculations as discussed in section 2.1. We shall show that in such a temperature range the above dependences can be understood within the single-ion crystal-field model of magnetostriction for itinerant magnets [1]. We could naturally extend our model to the whole interval $0.35 \leq x \leq 0.40$, but the lack of INS data makes this task unfeasible.

2. Model of single-ion magnetostriction for fluctuating-valence systems

The model developed consists of three stages:

(i) the determination of the Ce^{3+} -ion crystal energy levels and wavefunctions in the presence of an applied magnetic field, assuming some degree of itineracy because of the 4f-conduction electron band hybridization;

(ii) the calculation of the single-crystal irreducible equilibrium strains $\epsilon^{\alpha,1}$ and $\epsilon^{\alpha,2}$ for the itinerant system;

(iii) the calculation of ω and λ_t for *polycrystalline* samples, in order to compare our model results with the available experimental data, in this way obtaining the magnetoelastic coupling parameters.

We should note that $Ce(Ni_{1-x}Co_x)Sn$ intermetallics show unusually large magnetostrictions among the rare-earth unstable 4f-shell intermetallics [11, 12]. Therefore understanding the origin of the magnetoelastic coupling for the present FV compounds is of considerable interest.

Some previous considerations are of interest, as fully described elsewhere [1]. Our calculations will be done within the tight-binding approximation, using the usual Bloch functions $|\mathbf{k}\rangle$ with amplitudes $\phi_\lambda(\mathbf{r} - \mathbf{l}) \equiv |\lambda\rangle \equiv |m_J\rangle$, corresponding to the magnetic quantum number m_J , the projection of the angular momentum $J = 5/2$. \mathbf{k} and \mathbf{l} are the electron wavevector and the lattice site, respectively. It is a well known result [13–15] that the main contribution to the magnetoelastic coupling comes from those regions of the BZ where the symmetry is sufficiently high. This enormously simplifies the magnetostriction calculation, because such regions are in fact reduced to a few points of high symmetry in the BZ. Also, in order to have magnetostriction, those states must be degenerate, and this degeneration is lifted by the Zeeman interaction as we shall see in section 2.1. An additional condition must be fulfilled, and it is that the energy of those high-symmetry Bloch states should be sufficiently close to the Fermi level. This condition is required because, within our approach, the orbital magnetic moment is not quenched for the states in those \mathbf{k} regions, and it is completely quenched elsewhere, even in the presence of strong spin-orbit coupling. This quenching is well known to be due to interband site hopping. Our basis functions of one-electron states are the six $4f^1 |m_J\rangle$ states with $m_J = \pm 5/2, \pm 3/2, \pm 1/2$. An even further simplification is to consider only a single \mathbf{k} point in the BZ. As we shall see, our crystalline cell has a pseudo-tetragonal symmetry, and also the BZ; then some particular \mathbf{k} point within the BZ axis and close to the Fermi surface wavevector \mathbf{k}_F would probably be the most important in determining the magnetoelastic coupling interaction.

2.1. The Ce^{3+} -ion model Hamiltonian and energy levels

The hybridized 4f-conduction electron Hamiltonian H at site \mathbf{l} is modelled in the following way:

$$H = H_{CF} + H_z + H_{me} + H_{el} \quad (1)$$

where the different Hamiltonians are as follows. Because they are referred to a single ion, they are translationally invariant and therefore the matrix elements $\langle \mathbf{k}'; \lambda' | H | \mathbf{k}; \lambda \rangle$ are \mathbf{k} independent; hence we can treat H as a localized-electron Hamiltonian. For the CEF Hamiltonian we shall initially take that corresponding to orthorhombic symmetry [16]. This Hamiltonian can be considerably simplified if we take into account the following experimental results. Basal plane anisotropy should be small because in $CeNiSn$ the low-field susceptibilities measured along the a and b crystalline axes are similar [17]; the

magnetic anisotropy at a high field (14 T), derived from magnetization measurements on free and fixed single-grain powders, is weak [18]. Also, as mentioned before, for the range of Co concentrations at present considered, the basal plane lattice parameters $a \simeq b$. Those results agree well with the above-mentioned observation of only two INS peaks at 55 K for $x = 0.38$ [4]. All these results allow us to consider a *pseudo-tetragonal* symmetry with null basal plane (a, b) anisotropy and take

$$H_{CF} = B_{20}O_2^0 + B_{40}O_4^0 \quad (2)$$

where O_2^0 and O_4^0 are Stevens operators [19] and B_{n0} are CEF parameters. The basis functions for Hamiltonian (2) are the three doublets $|\pm 5/2\rangle$, $|\pm 3/2\rangle$ and $|\pm 1/2\rangle$. The corresponding energy levels ϵ_λ can be determined from the above INS data at 55 K. First of all, INS performed on the isomorphous compound CePtSn shows that the ground state (GS) is the $|\pm 3/2\rangle$ doublet [20]. Considering the selection rules for magnetic dipole transitions, the CEF energy level scheme deduced for the Ce^{3+} ion is $\epsilon_{\pm 1/2} = 16.35$ meV, $\epsilon_{\pm 3/2} = -25.73$ meV and $\epsilon_{\pm 5/2} = 9.38$ meV, the energies being measured from the unperturbed multiplet $|J = 5/2\rangle$. The CEF parameters obtained are $B_{20} = 0.142$ meV/ Ce^{3+} and $B_{40} = 0.086$ meV/ Ce^{3+} , not far from those of CePtSn [20]. The Zeeman Hamiltonian in the presence of an applied field \mathbf{H} is the usual Hamiltonian (1).

The magnetoelastic coupling Hamiltonian, assuming only that the modes $\epsilon^{\alpha,1}$ and $\epsilon^{\alpha,2}$ are active, is given by [10]

$$H_{me} = -M_{11}^\alpha \mathbf{J}^2 \epsilon^{\alpha,1} - M_{21}^\alpha \mathbf{J}^2 \epsilon^{\alpha,2} - \frac{\sqrt{3}}{2} M_{12}^\alpha O_2^0 \epsilon^{\alpha,1} - \frac{\sqrt{3}}{2} M_{22}^\alpha O_2^0 \epsilon^{\alpha,2} \quad (3)$$

where M_{ij}^α are single-ion magnetoelastic parameters. Finally the elastic Hamiltonian in terms of the pseudo-tetragonal symmetry elastic stiffness constants C_{ij}^α can be found in [10].

It should be noted that no exchange interaction between the 4f band and the Ni and Co 3d bands has been included in the Hamiltonian (2). The reason is that Ni does not have any magnetic moment in the present phases [18] and Co appears as paramagnetic according to magnetostriction measurements performed in the isomorphous compound $\text{La}(\text{Ni}_{0.65}\text{Co}_{0.35})\text{Sn}$ [4]. Therefore the Co and Ni sublattices are quite unable to polarize the 4f band through an eventual exchange mean field.

The Hamiltonian (1) was diagonalized for \mathbf{H} parallel to the c axis and within the basal plane. In the first case it is diagonal; for $\mathbf{H} \perp c$ it is not but, because the CEF energy is much larger than the Zeeman energy at the applied field (14 T), we have neglected the off-diagonal Zeeman matrix elements except those within the $|\pm 1/2\rangle$ Hamiltonian matrix box. In this way it is straightforward to show that the Ce^{3+} -ion energy levels are as follows.

For $\mathbf{H} \parallel c$,

$$E_{\pm 5/2} = \epsilon_{\pm 5/2} \pm \left(-\frac{15}{7}\right) \mu_B H_c + 5 \sum_{i=1}^2 M^{\alpha,i} \epsilon^{\alpha,i} \quad (4a)$$

$$E_{\pm 3/2} = \epsilon_{\pm 3/2} \pm \left(-\frac{9}{7}\right) \mu_B H_c - \sum_{i=1}^2 M^{\alpha,i} \epsilon^{\alpha,i} \quad (4b)$$

$$E_{\pm 1/2} = \epsilon_{\pm 1/2} \pm \left(-\frac{3}{7}\right) \mu_B H_c - 4 \sum_{i=1}^2 M^{\alpha,i} \epsilon^{\alpha,i} \quad (4c)$$

where the upper and lower signs correspond on both sides of equation (4). We have defined the effective magnetoelastic parameters

$$M^{\alpha,1} = - \left[\frac{35}{4} M_{11}^\alpha + \sqrt{3} M_{12}^\alpha \right] \quad M^{\alpha,2} = - \left[\frac{35}{4} M_{21}^\alpha + \sqrt{3} M_{22}^\alpha \right]. \quad (5)$$

For $\mathbf{H} \perp c$ (a, b plane),

$$E_{\pm 5/2} = \epsilon_{\pm 5/2} + 5 \sum_{i=1}^2 M^{\alpha,i} \epsilon^{\alpha,i} \quad (6a)$$

$$E_{\pm 3/2} = \epsilon_{\pm 3/2} - \sum_{i=1}^2 M^{\alpha,i} \epsilon^{\alpha,i} \quad (6b)$$

$$E_{\pm 1/2} = \epsilon_{\pm 1/2} \pm \left(-\frac{3}{7}\right) \mu_B H_a - 4 \sum_{i=1}^2 M^{\alpha,i} \epsilon^{\alpha,i}. \quad (6c)$$

2.2. Calculation of the irreducible magnetostrictive strains

The total energy of the Ce-ion sublattice is given by

$$U = U_{mel} + U_{el}. \quad (7)$$

The unit-volume magnetoelastic energy is given, for electrons of energy ϵ , by

$$U_{mel} = \sum_{\lambda=\pm 1/2}^{\pm 5/2} \int_{-\infty}^{\infty} \rho_{\lambda}(\epsilon - E_{\lambda}) f_{FD}(\epsilon - \mu) d\epsilon \quad (8)$$

where ρ_{λ} is the λ -subband density of states and f_{FD} is the Fermi–Dirac distribution function. E_{λ} are the centres of the energy subbands, as given by equations (4) and (6). U_{el} is the elastic energy [10].

The equilibrium strains are obtained by minimization of U against $\epsilon^{\alpha,i}$, $i = 1, 2$, i.e.

$$\frac{\partial U}{\partial \epsilon^{\alpha,i}} = - \sum_{\lambda=\pm 1/2}^{\pm 5/2} \frac{\partial E_{\lambda}}{\partial \epsilon^{\alpha,i}} \int_{-\infty}^{\infty} \epsilon \rho'_{\lambda}(\epsilon - E_{\lambda}) f_{FD}(\epsilon - \mu) d\epsilon + C_{ii}^{\alpha} \epsilon^{\alpha,i} + C_{12}^{\alpha} \epsilon^{\alpha,k} = 0 \quad (9)$$

$i = 1, 2; k \neq i$

where $\rho' \equiv d\rho/d\epsilon$. We shall model our 4f-hybridized λ -band density of states by rectangular functions of width $2W_{\lambda}$, centred around E_{λ} . These widths were obtained from the widths at the HWHM of the INS lines at 55 K for $x = 0.38$ [4], amounting to $2W_{\pm 1/2} = 14.6$ meV, $2W_{\pm 3/2} = 4.4$ meV and $2W_{\pm 5/2} = 14.6$ meV. Then we shall have

$$\rho'(\epsilon - E_{\lambda}) = \frac{1}{2W_{\lambda}} [\delta(\epsilon - E_{\lambda} + W_{\lambda}) - \delta(\epsilon - E_{\lambda} - W_{\lambda})] \quad (10)$$

where δ is the Dirac delta function. Substitution of (10) in (9) yields the following system of linear equations:

$$- \sum_{\lambda=\pm 1/2}^{\pm 5/2} \left\{ \frac{1}{2W_{\lambda}} \left(\frac{\partial E_{\lambda}}{\partial \epsilon^{\alpha,i}} \right) \left[\frac{E_{\lambda} - W_{\lambda}}{1 + \exp(\beta(E_{\lambda} - W_{\lambda} - \mu))} - \frac{E_{\lambda} + W_{\lambda}}{1 + \exp(\beta(E_{\lambda} + W_{\lambda} - \mu))} \right] \right\} + C_{ii}^{\alpha} \epsilon^{\alpha,i} + C_{12}^{\alpha} \epsilon^{\alpha,k} = 0 \quad i = 1, 2; k \neq i \quad (11)$$

where $\beta \equiv 1/k_B T$. The solution of the system of equations (11) immediately gives the equilibrium irreducible strains

$$\epsilon^{\alpha,i} = - \frac{1}{\Delta^{\alpha}} \sum_{\lambda=\pm 1/2}^{\pm 5/2} \left(\left\{ C_{kk}^{\alpha} \frac{\partial E_{\lambda}}{\partial \epsilon^{\alpha,i}} - C_{12}^{\alpha} \frac{\partial E_{\lambda}}{\partial \epsilon^{\alpha,k}} \right\} n_{\lambda} \right) \quad i, k = 1, 2; i \neq k \quad (12)$$

where n_{λ} is the number of states within the λ subband, i.e.

$$n_{\lambda} = \frac{1}{2W_{\lambda}} \left[\frac{E_{\lambda} + W_{\lambda}}{1 + \exp(\beta(E_{\lambda} + W_{\lambda} - \mu))} - \frac{E_{\lambda} - W_{\lambda}}{1 + \exp(\beta(E_{\lambda} - W_{\lambda} - \mu))} \right]; \quad (13)$$

in equations (12), $\Delta^\alpha = C_{11}^\alpha C_{22}^\alpha - (C_{12}^\alpha)^2$. Equations (12) can be particularized for the applied magnetic field \mathbf{H} parallel and perpendicular to the pseudo-tetragonal c axis, as we saw before.

2.3. Calculation of the polycrystal volume and anisotropic magnetostrictions: magnetoelastic coupling parameters

Our experimental results [3] deal with *polycrystalline* samples, i.e. we dispose of the volume magnetostriction ω and anisotropic magnetostriction λ_t . In order to apply the theory for single crystals developed above, we should express ω and λ_t in terms of $\epsilon^{\alpha,1}$ and $\epsilon^{\alpha,2}$ for any direction of the applied field \mathbf{H} with respect to the crystal axes (a, b, c). This means the difficult task of diagonalizing Hamiltonian (1) for an arbitrary field direction, calculating $\epsilon^{\alpha,1}$ and $\epsilon^{\alpha,2}$ in each case, and averaging the strains for the polycrystal. This difficulty can be considerably reduced assuming the following reasonable simplification. We note that at an applied field of 14 T the Zeeman energies are at least one order of magnitude smaller than the CEF energies. Therefore, if we attach a frame (X, Y, Z) to the polycrystalline sample and if for example $OZ \parallel \mathbf{H}$, for the grains with their c axis between the ‘extreme’ values, i.e. with $c \parallel OZ$, and with $c \parallel OX$ and $c \parallel OY$, their *total* energies will differ very little from the extreme grain energies. This allows us to assume that only the extreme grains are relevant to the polycrystal magnetostriction calculation. We shall call ‘ Γ grains’ those with their c axis parallel to $\Gamma = X, Y, Z$ and disposed in the way schematically shown in figure 1. With this assumption we shall proceed to calculate ω and λ_t .

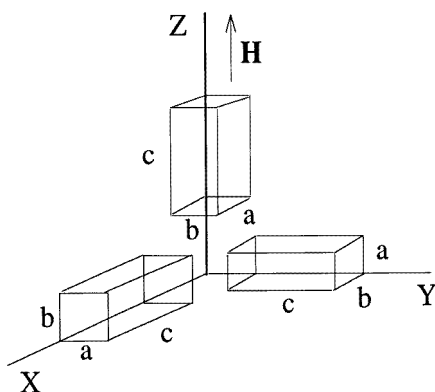


Figure 1. Schematic set-up showing the polycrystal attached frame (X, Y, Z), together with X, Y and Z types of grains, with indication of their single-crystal frame (a, b, c). The magnetic field \mathbf{H} is applied along the Z axis.

For $\mathbf{H} \parallel OZ$ the strains along the frame axes are

$$(\Delta l/l)_{\parallel OX} = \epsilon_{cc}(X) + \epsilon_{bb}(Y) + \epsilon_{aa}(Z) \quad (14a)$$

$$(\Delta l/l)_{\parallel OY} = \epsilon_{cc}(Y) + \epsilon_{aa}(X) + \epsilon_{bb}(Z) \quad (14b)$$

$$(\Delta l/l)_{\parallel OZ} = \epsilon_{cc}(Z) + \epsilon_{aa}(Y) + \epsilon_{bb}(X) \quad (14c)$$

where $\epsilon_{ii}(\Gamma)$, $i = a, b$ and c , are the ‘ Γ -grain’ Cartesian strains referred to the *crystal* frame (a, b, c). Considering that every Γ -frame axis is equally grain type populated, and assuming isotropy both within the grain basal plane (a, b) and within the (X, Y) plane, we

obtain the following strains for the polycrystalline sample:

$$(\Delta l/l)_{\parallel H} = \frac{1}{3}(\epsilon_{cc}(Z) + 2\epsilon_{aa}(X, Y)) \quad (15a)$$

$$(\Delta l/l)_{\perp H} = \frac{1}{3}(\epsilon_{cc}(X) + \epsilon_{aa}(X) + \epsilon_{aa}(Z)). \quad (15b)$$

Therefore for the *polycrystalline* grain ensemble we obtain, after straightforward manipulations, and in terms of the irreducible *crystal* strains, the following volume strain ω anisotropic strain λ_t :

$$\omega = (\Delta l/l)_{\parallel H} + 2(\Delta l/l)_{\perp H} = \frac{1}{3}(\epsilon^{\alpha,1}(\mathbf{H}\parallel\mathbf{c}) + 2\epsilon^{\alpha,1}(\mathbf{H}\parallel\mathbf{a})) \quad (16a)$$

$$\lambda_t = (\Delta l/l)_{\parallel H} - (\Delta l/l)_{\perp H} = \frac{\sqrt{3}}{3}\epsilon^{\alpha,2}(\mathbf{H}\parallel\mathbf{c}). \quad (16b)$$

In writing the last equality in equation (16b) we have considered that, because of the tetragonal symmetry, $\epsilon^{\alpha,2}(X) = -\epsilon^{\alpha,2}(Y)$. Note that, indeed, in equations (16) the Γ index becomes substituted by the conditions that the magnetic field is applied parallel to \mathbf{a} or \mathbf{c} . The strains (16) are given by equations (12) and (13), with the energy levels E_λ given by equations (4) and (6), obtaining

$$\omega = -\frac{1}{3\Delta_\alpha} \sum_{\lambda=\pm 1/2}^{\pm 5/2} \kappa_\lambda \langle \{ [C_{12}^\alpha M^{\alpha,2} - C_{22}^\alpha M^{\alpha,1}] n_\lambda \}_{H\parallel c} + 2 \{ [C_{12}^\alpha M^{\alpha,2} - C_{22}^\alpha M^{\alpha,1}] n_\lambda \}_{H\perp c} \rangle \quad (17a)$$

$$\lambda_t = -\frac{1}{\sqrt{3}\Delta_\alpha} \sum_{\lambda=\pm 1/2}^{\pm 5/2} \kappa_\lambda \langle \{ [C_{12}^\alpha M^{\alpha,1} - C_{11}^\alpha M^{\alpha,2}] n_\lambda \}_{H\parallel c} \rangle \quad (17b)$$

where $\kappa_{\pm 1/2} = 4$, $\kappa_{\pm 3/2} = 1$ and $\kappa_{\pm 5/2} = 5$.

3. Comparison with experimental results: magnetoelastic coupling parameters, discussion and conclusions

In figure 2 we present the thermal variation of the ω and the λ_t magnetostrictions for the compound $Ce(Ni_{0.62}Co_{0.38})Sn$ at an applied magnetic field of 14 T, once the magnetostrictions associated with the Co–Ni sublattice have been subtracted. So far we have not considered magnetostriction associated with the Co–Ni sublattice. The reason is that such magnetostriction is at least one order of magnitude smaller than that for Ce^{3+} , as shown by the compound $La(Ni_{0.65}Co_{0.35})Sn$ [4], where La is non-magnetic and hence its magnetostriction should be associated with the Co–Ni sublattice. As we mentioned before, magnetostriction isotherms in the above compound are quadratic with the applied magnetic field, indicating a paramagnetic state for the Co band. Although we have elsewhere [1] developed a model of magnetostriction for 3d-band ferromagnetic metals, we considered it more reliable, instead of calculating the magnetostrictions contributed by the paramagnetic Co–Ni sublattice, (with the introduction of additional fitting parameters), to subtract the corresponding La compound magnetostrictions and thus obtaining the Ce sublattice contributions, as shown in the above-mentioned figure 2. In fact, our main goal is to obtain the magnetoelastic parameters $M^{\alpha,1}$ and $M^{\alpha,2}$ associated with the Ce^{3+} ion in the present $Ce(Ni_{0.38}Co_{0.62})Sn$ compound.

In order to compare our model with the experimental magnetostriction results, a further simplification can be introduced. We note that the ratio ω/λ_t is approximately constant in the temperature range 50–170 K (figure 3). According to equations (17) this can be explained if only the GS subband $|\pm 3/2\rangle$ is populated, the remainder of the subbands

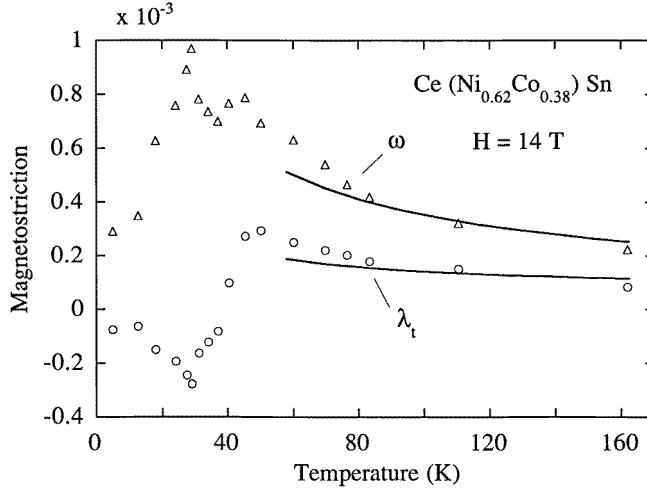


Figure 2. Thermal dependences of the volume magnetostrictions $\omega(\Delta)$ and anisotropic magnetostrictions λ_t (\circ) associated with the cerium sublattice, at an applied magnetic field of 14 T, for the $\text{Ce}(\text{Ni}_{0.62}\text{Co}_{0.38})\text{Sn}$ compound. The full curves are the theoretical model fits according to equations (18) (see section 3 for details).

being almost empty. This can happen if the following conditions are fulfilled, as in fact they are: the chemical potential μ is close to the GS; the applied magnetic field is strong enough to split the GS $|\pm 3/2\rangle$ doublet an energy greater than the band width $2W_{\pm 3/2}$; the next doublet $|\pm 1/2\rangle$ energy separation from the GS doublet (190 K) is smaller than the upper thermal excitation energy considered above (170 K) and also than the GS Zeeman energy (11.5 K); $2W_{\pm 3/2}$ is relatively narrow if compared with $2W_{\pm 1/2}$ and $2W_{\pm 5/2}$ (see section 2.3). Little is known about the elastic stiffness constants of the present series; for CeNiSn we know that $C_{11} = 1.3 \times 10^{12} \text{ erg cm}^{-3}$ and $C_{33} = 0.82 \times 10^{12} \text{ erg cm}^{-3}$ [21]. The symmetry elastic constants C_{ij}^{α} for pseudo-tetragonal symmetry are related to the Cartesian constants in the well known form [22].

We shall make a further approximation which consists in decoupling the $\epsilon^{\alpha,1}$ and $\epsilon^{\alpha,2}$ modes, i.e. we assume that $C_{12}^{\alpha} = 0$. With all the above assumptions, equations (17) are strongly simplified, i.e.

$$\omega = \frac{M^{\alpha,1}}{3C_{11}^{\alpha}} \sum_{\lambda=\pm 3/2} \{ \langle n_{\lambda} \rangle_{H\parallel c} + 2 \langle n_{\lambda} \rangle_{H\perp c} \} \quad (18a)$$

$$\lambda_t = \frac{M^{\alpha,2}}{\sqrt{3}C_{22}^{\alpha}} \sum_{\lambda=\pm 3/2} \langle n_{\lambda} \rangle_{H\parallel c}. \quad (18b)$$

In figure 2 we show the ‘best’ fit by equations (18) of the ω and λ_t thermal variations for the cerium sublattice contributions, in the interval 50–170 K, for the $\text{Ce}(\text{Ni}_{0.62}\text{Co}_{0.38})\text{Sn}$ compound. Choosing the lower-temperature boundary at 50 K we avoid the difficult problem which must arise if one wants to discuss the valence transition at T_v . It has been suggested that the single-site excitation of the Ce Kondo lattice [4], the electron–phonon interaction as in the BCS superconductors and/or the elastic constants softening could be responsible for the large magnetostriction increase above and near T_v [23]. The fitting parameters were $\mu = -22 \text{ meV}$ (measured from the centre of gravity of the $|J = 5/2\rangle$ multiplet), $M^{\alpha,1} = 0.7 \text{ meV/Ce}^{3+}$ ($\equiv 8 \text{ K/Ce}^{3+}$) and $M^{\alpha,2} = 4.6 \text{ meV/Ce}^{3+}$ ($\equiv 53 \text{ K/Ce}^{3+}$). The assumed

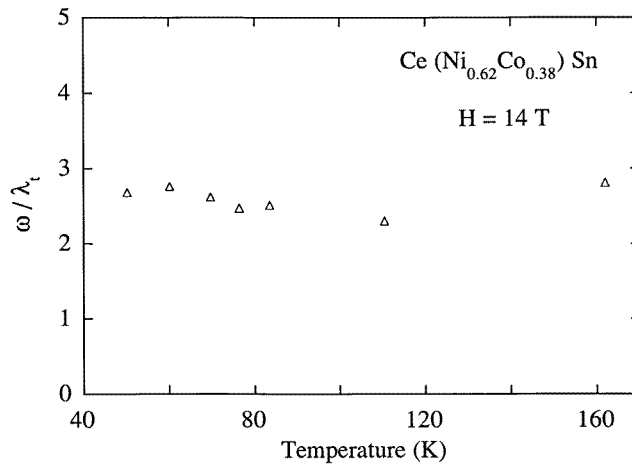


Figure 3. Thermal dependence of the ratio ω/λ_t of the volume magnetostriction to the anisotropic magnetostriction for the $Ce(Ni_{0.62}Co_{0.38})Sn$ compound, in the range 50–170 K and for an applied magnetic field of 14 T.

symmetry elastic constants were $C_{11}^\alpha = (1/9)(2C_{11} + C_{33})$ and $C_{22}^\alpha = (2/3)(C_{11} + 2C_{33})$, and therefore the above magnetoelastic parameters are only rough estimates (however, note that $M^{\alpha,i}/C_{ii}^\alpha$ are properly fitted). We can compare our magnetoelastic parameters with those for well magnetostrictively characterized intermetallics. For instance, for the cubic Laves phase intermetallics REM_2 (RE = rare earth), the tetragonal magnetoelastic parameter M_2^γ ranges between -5 and -11 K/RE $^{3+}$ (M = Ni) [24] and between -4 and -52 K/RE $^{3+}$ (M = Al) [25]; for the CsCl structure intermetallics CeM, M_2^γ takes the values 160 K/Ce $^{3+}$ (M = Zn) and 58 K/Ce $^{3+}$ (M = Ag) [26]. Therefore the overall conclusion is that the magnetoelastic coupling is *strong* for the present FV intermetallics. This result could in part justify the gigantic spontaneous volume magnetostrictive ‘jump’ ($\Delta\omega_s \approx 0.3$ – 2.5%) observed at the valence transition at T_v for $0.35 \leq x \leq 0.40$ [3, 4].

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