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Magnetoelastic interactions in the orthorhombic RECu₂ compounds (RE ≡ Tb, Dy, Ho, Er, Tm)

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Abstract. A model for the description of magnetoelastic interactions in orthorhombic RECu₂ intermetallic compounds is presented and compared with available experimental data on TmCu₂ and ErCu₂.

1. Introduction

A large amount of the experimental work has been done on the RECu₂ (RE ≡ rare earth) intermetallic compounds in the last decade [1–6]. The results of inelastic neutron scattering [2], neutron diffraction [3], magnetisation [4], susceptibility [5] and specific heat measurements [6] revealed a significant crystal-field (CF) splitting of the localised 4f states of the RE³⁺ ion.

Generally it was found that in cubic, hexagonal and tetragonal intermetallics the split states are related to the magnetoelastic lattice distortions even in the paramagnetic state of the particular compound (see, e.g., [7]). The corresponding magnetoelastic Hamiltonian acts as a perturbation on the CF states of the RE³⁺ ion and is usually written in terms of the tensor operators and elastic strains using the point group symmetry of the RE site [7]. This Hamiltonian allowed us to describe satisfactorily the thermal expansion, magnetostriction and sound velocity data of various RE intermetallics [8].

The magnetoelastic effects have been reported earlier for a few RECu₂ compounds [5, 6] even in the paramagnetic temperature range. The main reason for this work is to extend the usual concept of the magnetoelastic Hamiltonian written in terms of the tensor operators and elastic strains to the case of the RECu₂ compounds with orthorhombic symmetry and to discuss the connection with the experimental data now available.

2. Theoretical model

We assume that the RE³⁺ ion is influenced by the CF of orthorhombic symmetry. Since the energy separation between RE multiplets in the RE intermetallics is large in comparison with the splitting of multiplets due to the CF, the interaction between multiplets (*J*-mixing) can usually be neglected and the CF Hamiltonian may be written:

$$\begin{aligned} \mathcal{H}_{\text{CF}} = & V_2^0 O_2^0(J) + V_2^2 O_2^2(J) + V_4^0 O_4^0(J) + V_4^2 O_4^2(J) + V_4^4 O_4^4(J) \\ & + V_6^0 O_6^0(J) + V_6^2 O_6^2(J) + V_6^4 O_6^4(J) + V_6^6 O_6^6(J), \end{aligned} \quad (1)$$

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where V_n^m are the CF parameters and $O_n^m(J)$ are the Stevens equivalent operators (see, e.g., [5]).

This CF of low symmetry (C_{2v}) lifts the $2J + 1$ degeneracy of the ground-state multiplet into the set of doublet ($2J + 1$ even) and singlet ($2J + 1$ odd) levels. Even in the paramagnetic state the corresponding energy spectrum is perturbed by magnetoelastic interaction with the lattice strains. In the absence of magnetic order and structural transitions these strains are usually small and terms in the magnetoelastic coupling Hamiltonian which are linear in strain provide a reasonable approximation. Therefore we assume that the Hamiltonian \mathcal{H}_{ME} for one-ion magnetoelastic coupling fulfils symmetry requirements in the form [9]

$$\begin{aligned} \mathcal{H}_{\text{ME}} = & B_{10}^1 \varepsilon_{xx} O_2^0 + B_{11}^1 \varepsilon_{xx} O_2^2 + B_{20}^1 \varepsilon_{yy} O_2^0 + B_{21}^1 \varepsilon_{yy} O_2^2 + B_{30}^1 \varepsilon_{zz} O_2^0 \\ & + B_{31}^1 \varepsilon_{zz} O_2^2 + B^2 \varepsilon_{xy} (J_x J_y + J_y J_x) + B^3 \varepsilon_{xz} (J_x J_z + J_z J_x) \\ & + B^4 \varepsilon_{yz} (J_y J_z + J_z J_y). \end{aligned} \quad (2)$$

In this expression, the B_{ij}^k and B^k ($k = 1, 2, 3$ and 4) are nine magnetoelastic coefficients associated with the normal strain modes ε_{ab} ($a, b = x, y, z$) corresponding to the orthorhombic symmetry ($\varepsilon_{xx}, \varepsilon_{yy}, \varepsilon_{zz}$ for Γ_1 ; ε_{xy} for Γ_2 ; ε_{xz} for Γ_3 ; ε_{yz} for Γ_4) [9]. Let us consider that the term \mathcal{H}_{ME} gives only a small perturbation of the CF energy levels ($\Delta E_i/E_i \approx 10^{-4}$) in the RECu₂ compounds in the paramagnetic temperature range. Also the values of the Debye temperatures within the RECu₂ series ($\Theta_D \approx 200$ K [5, 6]) suggest that the elastic strains are small. Then in (2) we can limit ourselves to the second-order terms in the total angular momentum operators J_x, J_y, J_z and the elastic energy can be written as [10]

$$\begin{aligned} E_{\text{el}} = & \frac{1}{2}(c_{11} \varepsilon_{xx}^2 + c_{22} \varepsilon_{yy}^2 + c_{33} \varepsilon_{zz}^2) + c_{12} \varepsilon_{xx} \varepsilon_{yy} + c_{13} \varepsilon_{xx} \varepsilon_{zz} \\ & + c_{23} \varepsilon_{yy} \varepsilon_{zz} + c_{44} \varepsilon_{yz}^2 + c_{55} \varepsilon_{xz}^2 + c_{66} \varepsilon_{xy}^2 \end{aligned} \quad (3)$$

where c_{ij} are nine independent elastic constants for the orthorhombic symmetry. The total Hamiltonian \mathcal{H} acting on the ground-state multiplet of the RE³⁺ ion is

$$\mathcal{H} = \mathcal{H}_{\text{CF}} + \mathcal{H}_{\text{ME}} + E_{\text{el}}. \quad (4)$$

Minimising the free energy with respect to the strains leads to the following equilibrium values for the normal strain modes:

$$\begin{aligned} \varepsilon_{xx} &= A_{xx} \langle O_2^0 \rangle + B_{xx} \langle O_2^2 \rangle & \varepsilon_{yz} &= A_{yz} \langle (J_y J_z + J_z J_y) \rangle \\ \varepsilon_{yy} &= A_{yy} \langle O_2^0 \rangle + B_{yy} \langle O_2^2 \rangle & \varepsilon_{xz} &= A_{xz} \langle (J_x J_z + J_z J_x) \rangle \\ \varepsilon_{zz} &= A_{zz} \langle O_2^0 \rangle + B_{zz} \langle O_2^2 \rangle & \varepsilon_{xy} &= A_{xy} \langle (J_x J_y + J_y J_x) \rangle \end{aligned} \quad (5)$$

where the coefficients A_{ab} and B_{ab} are rather tedious functions of the magnetoelastic coefficients B_{ij}^k and B^k and the elastic constants c_{ij} . $\langle O_2^0 \rangle$ and $\langle O_2^2 \rangle$ mean

$$\begin{aligned} \langle O_2^0 \rangle &= \sum_i \mu_i \exp(-E_i/k_B T) / \sum_i \exp(-E_i/k_B T) \\ \langle O_2^2 \rangle &= \sum_i \nu_i \exp(-E_i/k_B T) / \sum_i \exp(-E_i/k_B T) \end{aligned} \quad (6)$$

where $\mu_i = \langle \Gamma_i | O_2^0 | \Gamma_i \rangle$, $\nu_i = \langle \Gamma_i | O_2^2 | \Gamma_i \rangle$ are the matrix elements of the second-order operators O_2^0 and O_2^2 within the CF states Γ_i of the RE³⁺ ion. Neglecting the terms

quadratic in ε_{ab} the change in lattice parameters a , b and c can be expressed in terms of the equilibrium strains (5) in the form $\varepsilon_{xx} = \Delta c/c$, $\varepsilon_{yy} = \Delta a/a$ and $\varepsilon_{zz} = \Delta b/b$. The temperature dependence of lattice parameters is then given by the temperature behaviour of $\langle O_2^0 \rangle$ and $\langle O_2^2 \rangle$.

We are interested in the thermal change $\delta V/V$ in volume which is the first invariant of the small strain tensor ε_{ab} and the thermal volume expansion coefficient β_{CF} which is the temperature derivative of $\delta V/V$:

$$\begin{aligned} \delta V/V &= \varepsilon_{xx} + \varepsilon_{yy} + \varepsilon_{zz} \\ &= (A_{xx} + A_{yy} + A_{zz})\langle O_2^0 \rangle + (B_{xx} + B_{yy} + B_{zz})\langle O_2^2 \rangle \\ &= \mathcal{A}\langle O_2^0 \rangle + \mathcal{B}\langle O_2^2 \rangle \end{aligned} \quad (7)$$

$$\begin{aligned} \beta_{CF} &= d(\delta V/V)/dT \\ &= d(\varepsilon_{xx} + \varepsilon_{yy} + \varepsilon_{zz})/dT \\ &= (1/k_B T^2)[\mathcal{A}(\langle O_2^0 E \rangle - \langle O_2^0 \rangle \langle E \rangle) + \mathcal{B}(\langle O_2^2 E \rangle - \langle O_2^2 \rangle \langle E \rangle)] \end{aligned} \quad (8)$$

where $\mathcal{A} = A_{xx} + A_{yy} + A_{zz}$, $\mathcal{B} = B_{xx} + B_{yy} + B_{zz}$ and k_B is the Boltzmann constant. We see that the values of volume change $\delta V/V$ and thermal expansion coefficient β_{CF} are simply related to the mean values of the second-order operators $\langle O_2^0 \rangle$ and $\langle O_2^2 \rangle$.

3. Comparison with experimental data

In the RECu₂ series the CF part of the thermal expansion coefficient β_{CF} can be found in [6] (RE \equiv Tb, Dy, Ho, Er) and in [5] for TmCu₂. The two most important compounds for our purpose are ErCu₂ and TmCu₂ where the CF contribution to the thermal expansion is not masked by magnetic ordering owing to their low ordering temperatures (11.2 K and 6.3 K, respectively [5, 6]) and the phonon and electronic parts can be easily subtracted. In the other RECu₂ (RE \equiv Tb, Dy, Ho) compounds the CF part of their thermal expansion cannot be simply separated owing to their higher ordering temperatures. For this reason in the following we take into consideration the experimental data for ErCu₂ [6] and TmCu₂ [5] compounds only.

The characteristic feature of the $\beta_{CF}-T$ curve is a deep broad minimum near 30 K (figures 1 and 2). The CF origin of this feature seems to be confirmed by comparison with non-magnetic YCu₂ where the total thermal expansion coefficient consists of the phonon and electronic parts only and no similar minimum was observed [5].

The detailed quantitative analysis of these experimental data requires the values of the CF parameters V_n^m . To our best knowledge such values for RECu₂ compounds are unknown as yet. The only values available are the realistic estimates for V_2^0 and V_2^2 based on the analysis of the experimental temperature dependence of susceptibility [1, 5] and the qualitative values for V_n^m ($n > 2$) from the analysis of additional thermodynamic properties of TmCu₂ [5]. To provide at least a qualitative analysis of $\beta_{CF}-T$ curves in the framework of our model we have calculated $d(\langle O_2^0 \rangle)/dT$ and $d(\langle O_2^2 \rangle)/dT$ using the above-mentioned estimates of the CF parameters [5] (figures 1 and 2).

The temperature dependences of $d(\langle O_2^0 \rangle)/dT$ exhibit similar features to the $\beta_{CF}-T$ curves, the pronounced minimum near 30 K in particular (figures 1 and 2). The details of curvature in both cases depend on the values of CF parameters but the basic features seem to be the same.

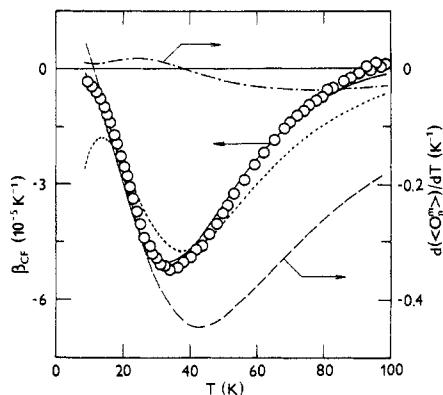


Figure 1. Temperature dependence of the thermal expansion coefficient for TmCu_2 (\circ) in comparison with the $d\langle O_2^0 \rangle / dT$ (---) and $d\langle O_2^2 \rangle / dT$ (- · - ·): —, fit using the CF parameter set number 6 from [5] which provides the best agreement with the experimental data. For comparison we also show the fit using the CF parameter set number 1 [5] (····) which is the worst fit (see table 1).

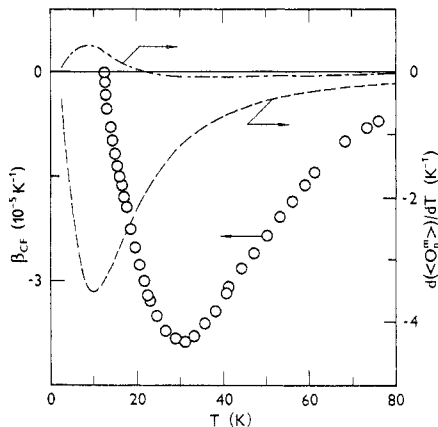


Figure 2. Temperature dependence of the thermal expansion coefficient for ErCu_2 (\circ) in comparison with the $d\langle O_2^0 \rangle / dT$ (---) and $d\langle O_2^2 \rangle / dT$ (- · - ·). The $d\langle O_2^0 \rangle / dT$ and $d\langle O_2^2 \rangle / dT$ dependences were calculated using $V_0^2 = -0.48 \times 10^{-23} \text{ J ion}^{-1}$ and $V_2^2 = -0.49 \times 10^{-23} \text{ J ion}^{-1}$ [1].

Table 1. The fitted coefficients \mathcal{A} and \mathcal{B} according to (8) for TmCu_2 with CF parameter sets [5] (χ^2 is the relative mean square deviation).

Parameter set number	\mathcal{A} (10^{-5})	\mathcal{B} (10^{-4})	χ^2
1	12	-11	7.06
2	20	-17	1.22
3	6	-5	1.86
4	11	-5	1.29
5	12	-6	1.04
6	11	-6	0.69

For the quantitative analysis, at least the qualitative estimates of the higher-order CF parameters ($n > 2$) (e.g. from [5]) must be used to obtain agreement with the experiment. This could be done in the case of TmCu_2 using equation (8) and good agreement with the experimental data can be observed (figure 1). The fitted values of coefficients \mathcal{A} and \mathcal{B} are collected in table 1.

In the case of ErCu_2 , where we can use the estimates for the second-order parameters only, such agreement cannot be obtained. For the comparison we have also calculated the dependences of $d\langle O_2^0 \rangle / dT$ and $d\langle O_2^2 \rangle / dT$ for TmCu_2 using second-order parameters only. Also, in this case, quantitative agreement with the experiment cannot be observed. This feature reflects the importance of higher-order CF parameters for similar calculations in the framework of our model.

4. Discussion

We have used standard theory for calculating the magnetoelastic strains and developed the approach to include orthorhombic symmetry as well. The presented model allows us to treat the various magnetoelastic effects for the orthorhombic RECu₂ compounds in a systematic way. In particular we have shown that the temperature anomalies in the coefficient of thermal expansion can be interpreted in terms of the temperature dependence of $d(\langle O_2^0 \rangle)/dT$, $d(\langle O_2^2 \rangle)/dT$ of the RE ion. Therefore the introduction of the independent CF Grüneisen parameters [5, 6] is unnecessary. The model is also capable of describing the magnetostriction and magnetic field dependence of the sound velocity data. This can be done by adding the appropriate magnetic-field-dependent term into the total Hamiltonian (4).

On the other hand it is to be noted that we have omitted quadrupole–quadrupole interactions in our approach. These interactions were shown to play an important role in the magnetically ordered state or in the vicinity of the structural transitions [7]. In the paramagnetic temperature range and in the absence of structural transition, however, the quadrupole–quadrupole interactions are small and can usually be well described within the molecular-field approximation. The corresponding Hamiltonian has then exactly the same form as the magnetoelastic Hamiltonian and perturbation of the CF energy levels is negligible [7].

We wish also to point out that in the magnetoelastic Hamiltonian (2) we have neglected all quadratic and higher-order terms in elastic strains and second-order operators. Once again, these terms do not play a significant role in the paramagnetic region.

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