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The influence of the crystal field on the anisotropic thermal expansion in $ErCu_2$ and $NdCu_2$

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Abstract. The anisotropic thermal expansion parameters $a(T)$, $b(T)$ and $c(T)$ of some $RECu_2$ intermetallics (RE = Y, Er, Nd) has been measured in the temperature range from 400 K down to 4.2 K using x-ray powder diffraction. The influence of the crystal field on the thermal expansion in $ErCu_2$ and $NdCu_2$ has been determined by comparing the thermal expansion of the non-magnetic isostructural YCu_2 with the Er and Nd compounds. The data thus obtained are described theoretically using a set of crystal-field parameters deduced from the analysis of inelastic neutron diffraction data.

1. Introduction

The intermetallic $RECu_2$ compounds crystallize in the orthorhombic $CeCu_2$ type of structure (space group D_{2h}^{28} (*Imma*)). More than ten years ago Hashimoto (1979) showed that the crystal field (CF) is of considerable importance for the magnetic properties of the $RECu_2$ compounds. In a number of recent publications the influence of the CF has been investigated in these low-symmetry compounds. The intermetallic compounds $CeCu_2$ (Gratz *et al* 1985), $SmCu_2$ (Gratz *et al* 1990), $NdCu_2$ (Gratz *et al* 1991), $ErCu_2$ (Gubbens *et al* 1991) and $TmCu_2$ (Zajac *et al* 1988) have been studied by various physical methods (neutron scattering, field dependent magnetization, specific heat, thermal expansion and transport properties). Due to the low symmetry of these compounds it is difficult to determine the whole set of nine crystal-field parameters from the experiments. These difficulties have partly been overcome by the theoretical investigations of Newman (1983) and Divis (1991). They showed that within some approximations the number of parameters can be reduced. For the compounds $ErCu_2$ and $NdCu_2$, sets of crystal-field parameters have been given by Gubbens *et al* (1991) and Gratz *et al* (1991).

The aim of this paper is to show the temperature variation of the lattice parameters a, b and c in $ErCu_2$, $NdCu_2$, and YCu_2 determined by x-ray powder diffraction in the temperature range from 4.2 K to 400 K. The observed anomalies in $a(T)$, $b(T)$ and $c(T)$ at lower temperatures in $ErCu_2$ and $NdCu_2$ are due to the crystal-field influence and can well be described with the above-mentioned sets of parameters.

The temperature variation of a, b and c of YCu_2 (which is non-magnetic and isostructural with $ErCu_2$ and $NdCu_2$) is used as a reference for the experimental determination of the crystal-field influence in the Er and Nd compounds.

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2. Sample preparation and experimental techniques

Polycrystalline samples of $ErCu_2$, $NdCu_2$ and YCu_2 have been prepared by induction melting under a protective argon atmosphere. After annealing at 700 °C for one week no trace of foreign phases has been found.

A conventional Siemens D500 diffractometer with Co Kα radiation has been used for the measurements of the lattice parameters (a, b, c) as a function of temperature. The room temperature sample holder of the diffractometer has been replaced by an Oxford He-flow cryostat which operates in the temperature range from about 4 K up to 500 K.

3. Results and discussion

The temperature dependence of the lattice parameters a, b and c of the three isostructural $RECu_2$ compounds (RE = Er, Nd, Y), measured from 4.2 K up to 400 K (300 K), is shown in figure 1. (To avoid oxidation during the measuring procedure we limited the upper temperature to 300 K in the case of $NdCu_2$.) These parameters are normalized to the values at 400 K (300 K). The lattice parameters at room temperature (300 K) are listed in table 1.

Table 1. Lattice parameters of $ErCu_2$, $NdCu_2$ and YCu_2 at 300 K.

$RECu_2$	a (Å)	b (Å)	c(Å)
$ErCu_2$	4.275 ± 0.001	6.748 ± 0.003	7.267 ± 0.003
$NdCu_2$	4.385 ± 0.001	7.036 ± 0.006	7.421 ± 0.002
YCu_2	4.301 ± 0.001	6.874 ± 0.003	7.297 ± 0.001

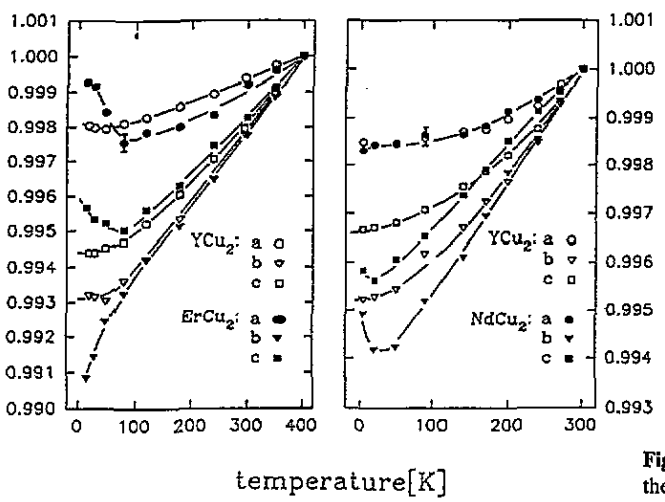

Figure 1. Temperature dependence of the normalized lattice parameters of YCu_2, $ErCu_2$ and $NdCu_2$.

For the calculation of the crystal-field contribution to the thermal expansion we assumed that the free energy $F(T, \epsilon)$ consists of a lattice and an electron part

denoted by $F_0(T,\epsilon)$ and (for $ErCu_2$ and $NdCu_2$) a magnetic part $F_{mag}(T,\epsilon)$. Here T is the absolute temperature and ϵ denotes the strain tensor.

$$F(T,\epsilon) = F_0(T,\epsilon) + F_{mag}(T,\epsilon). \tag{1}$$

The model used for the calculation of $F_{mag}(T,\epsilon)$ is based on the single-ion crystal-field Hamiltonian

$$H_{cf}(\epsilon=0) = V_2^0 O_2^0(J) + V_2^2 O_2^2(J) + V_4^0 O_4^0(J) + V_4^2 O_4^2(J) + V_4^4 O_4^4(J) + V_6^0 O_6^0(J) + V_6^2 O_6^2(J) + V_6^4 O_6^4(J) + V_6^6 O_6^6(J) \tag{2a}$$

where V_i^j are the crystal-field parameters, O_l^m the Stevens operators and J the total angular momentum quantum number, and the magnetoelastic Hamiltonian for orthorhombic symmetry (Zvezdin *et al* 1985)

$$H_{me}(\epsilon) = \sum_{i=1}^{3} \epsilon_i (B_{i0}^1 O_2^0 + B_{i1}^1 O_2^2) + B^2\epsilon_4(J_1J_2 + J_2J_1) + B^3\epsilon_5(J_1J_3 + J_3J_1) + B^4\epsilon_6(J_2J_3 + J_3J_2) \tag{2b}$$

where $B_{i0}^1, B_{i1}^1, B^2, B^3, B^4$ are the magnetoelastic coupling parameters, $\epsilon_1,\ldots,\epsilon_6$ the components of the strain tensor and J_i the components of the total angular momentum operator.

H_{me} describes the coupling of the crystal field to the lattice and therefore the resulting strains. It is obtained by a series expansion of H_{cf} with respect to ϵ, where H_{me} is the linear term.

The magnetic contribution F_{mag} to the free energy is now given by

$$F_{mag}(T,\epsilon) = N\sum_{\nu}(\exp(-E_\nu/kT)/Z)\langle\Gamma_\nu|H_{cf}(\epsilon=0) + H_{me}(\epsilon)|\Gamma_\nu\rangle = \langle H_{cf}(\epsilon=0) + H_{me}(\epsilon)\rangle_T \tag{3}$$

where E_ν and $|\Gamma_\nu\rangle$ are the eigenvalues and eigenstates of $H_{cf}(\epsilon=0)$, respectively. N denotes the number of rare earth atoms per unit volume.

Using equation (1) and the well known formula to calculate stresses σ_i and elastic constants c_{ij} (see e.g. Barron *et al* 1980)

$$\sigma_i(T,\epsilon) = (1/V)\partial F/\partial\epsilon_i \qquad c_{ij}(T,\epsilon) = (1/V)\partial^2 F/\partial\epsilon_i\partial\epsilon_j \qquad i,j = 1,\ldots,6 \tag{4}$$

and neglecting terms of order ϵ^2 it is possible to write $\sigma(T,\epsilon)$ as

$$\sigma_i(T,\epsilon) = \sigma_i^0(T,\epsilon=0) + \sigma_i^{mag}(T,\epsilon=0) + \sum_{j=1}^{6} c_{ij}\epsilon_j. \tag{5}$$

Because of the orthorhombic symmetry the c_{ij} with $i \leqslant 3$ and $j \geqslant 4$ vanish. The three equations (5) for $i = 1,2,3$ can be inverted to obtain the $\epsilon_i(T,\sigma)$ $(i = 1,2,3)$. The temperature dependence of ϵ at zero stress σ now reads

$$\epsilon_i(T) = \sum_{j=1}^{3} s_{ij}[\sigma_j^0(T,\epsilon=0) + \sigma_j^{mag}(T,\epsilon=0)] = \epsilon_i^0(T) + \epsilon_i^{mag}(T). \tag{6}$$

Here the s_{ij} are the elastic compliances (Barron *et al* 1980) and

$$\epsilon_i^0(T) = -(1/V)\sum_{j=1}^{3} s_{ij}\frac{\partial F}{\partial \epsilon_j^0}.$$

Using equations (1)–(3) the strain components ϵ_i^{mag} are given by

$$\epsilon_i^{mag} = -(1/V)\sum_{j=1}^{3} s_{ij}\frac{\partial F}{\partial \epsilon_j^{mag}} = \mathbb{A}_i\langle O_2^0\rangle_T + \mathbb{B}_i\langle O_2^2\rangle_T \qquad i = 1,2,3 \tag{7}$$

with

$$\mathbb{A}_i = -(N/V)\sum_{j=1}^{3} s_{ij}B_{j1}^1 \qquad \mathbb{B}_i = -(N/V)\sum_{j=1}^{3} s_{ij}B_{j0}^1.$$

Because neither the non-magnetic contribution $F_0(T)$ to the free energy nor the strain components $\epsilon_i^0(T)$ of the magnetic compound are known, it is necessary to determine them from the measurement of an isostructural non-magnetic 'reference' compound (YCu_2).

In the following $a_i(T)$ $(i = 1,2,3)$ denote the temperature dependent lattice parameters of the magnetic compound ($ErCu_2$ or $NdCu_2$) and the $r_i(T)$ are the lattice parameters of YCu_2. For the following calculation we subdivide $a_i(T)$ (and $r_i(T)$) into a temperature independent part $a_i^0, (r_i^0)$ and a temperature dependent part $\Delta a_i(T)$, $(\Delta r_i(T))$:

$$a_i(T) = a_i^0 + \Delta a_i(T) \qquad r_i(T) = r_i^0 + \Delta r_i(T). \tag{8}$$

Now the difference of the lattice parameters, normalized to any temperature T_N, can be written as:

$$\begin{aligned} a_i(T)/a_i(T_N) - r_i(T)/r_i(T_N) \simeq [\Delta a_i(T) - \Delta a_i(T_N)]/a_i^0 - [\Delta r_i(T) \\ - \Delta r_i(T_N)]/r_i^0 = [\epsilon_i^a(T) - \epsilon_i^r(T)] - [\epsilon_i^a(T_N) - \epsilon_i^r(T_N)]. \end{aligned} \tag{9}$$

If we assume that the strain of the reference compound ϵ_i^r represents the non-magnetic contribution ϵ_i^0 to the total strain of the magnetic compound in equation (6), then equation (8) can be written in the following form:

$$\begin{aligned} a_i(T)/a_i(T_N) - r_i(T)/r_i(T_N) = \epsilon_i^{mag}(T) - \epsilon_i^{mag}(T_N) = \mathbb{A}_i(\langle O_2^0\rangle_T - \langle O_2^0\rangle_{T_N}) \\ + \mathbb{B}_i(\langle O_2^2\rangle_T - \langle O_2^2\rangle_{T_N}). \end{aligned} \tag{10}$$

For the calculation of the expectation values at the variable temperature T $(\langle O_l^m\rangle_T)$ and at the normalization temperature T_N $(\langle O_l^m\rangle_{TN})$ in equation (10) we used the crystal-field parameters obtained from inelastic neutron scattering experiments ($NdCu_2$: Gratz *et al* 1991; $ErCu_2$: Gubbens *et al* 1991). The values are listed in table 2. Since for the $RECu_2$ compounds the elastic and magnetoelastic constants which determine the coefficients $\mathbb{A}_i$ and $\mathbb{B}_i$ are not known, it was necessary to determine these coefficients by fitting the model (equation (10)) to the experimental

Table 2. Crystal-field parameters for $ErCu_2$ and $NdCu_2$ (K).

$NdCu_2$:			
$V_2^0 = 1.35$	$V_2^2 = 1.56$		
$V_4^0 = 2.23 \times 10^{-2}$	$V_4^2 = 1.01 \times 10^{-2}$	$V_4^4 = 1.96 \times 10^{-2}$	
$V_6^0 = 5.52 \times 10^{-4}$	$V_6^2 = 1.35 \times 10^{-4}$	$V_6^4 = 4.89 \times 10^{-4}$	$V_6^6 = 4.25 \times 10^{-3}$
$ErCu_2$:			
$V_2^0 = -0.28$	$V_2^2 = -0.22$		
$V_4^0 = -0.30 \times 10^{-2}$	$V_4^2 = -0.14 \times 10^{-2}$	$V_4^4 = 0.30 \times 10^{-2}$	
$V_6^0 = -0.20 \times 10^{-4}$	$V_6^2 = -0.47 \times 10^{-4}$	$V_6^4 = -0.97 \times 10^{-4}$	$V_6^6 = -2.96 \times 10^{-4}$

Table 3. Fitted values $\mathbb{A}_i$ and $\mathbb{B}_i$ for $ErCu_2$ and $NdCu_2$.

RECu_2	$\mathbb{A}_1$	$\mathbb{A}_2$	$\mathbb{A}_3$	$\mathbb{B}_1$	$\mathbb{B}_2$	$\mathbb{B}_3$
$ErCu_2$	3×10^{-5}	3×10^{-5}	5×10^{-6}	-7×10^{-4}	2×10^{-4}	3×10^{-4}
$NdCu_2$	-5×10^{-5}	7×10^{-5}	-8×10^{-6}	-5×10^{-5}	3×10^{-4}	2×10^{-4}

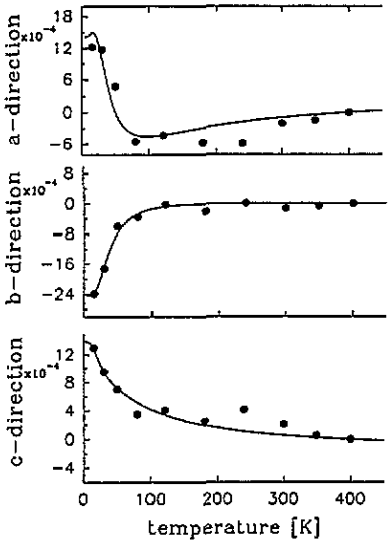

Figure 2. Experimentally determined differences of the normalized lattice parameters of $ErCu_2$ and YCu_2 (symbols). The lines represent the calculated results.

data. In table 3 we have listed the $\mathbb{A}_i$ and $\mathbb{B}_i$ values for which a least squares fit gave the best results.

In figures 2 and 3 the experimentally deduced influence of the crystal field on the thermal expansion in the three directions is given by the symbols. The lines in these figures show the theoretical results according to equation (10). It is obvious that the crystal-field influence is larger in $ErCu_2$ in comparison to $NdCu_2$. This may be attributed to the fact that the ground state in $ErCu_2$ is nearly a pure $|\pm 15/2\rangle$ Kramers doublet (as was suggested by Gubbens *et al* 1991), which strongly enhances $\langle O_2^0 \rangle_T$ at low temperatures.

4. Summary

The anisotropic thermal expansion of three RECu_2 compounds (RE = Y, Er, Nd)

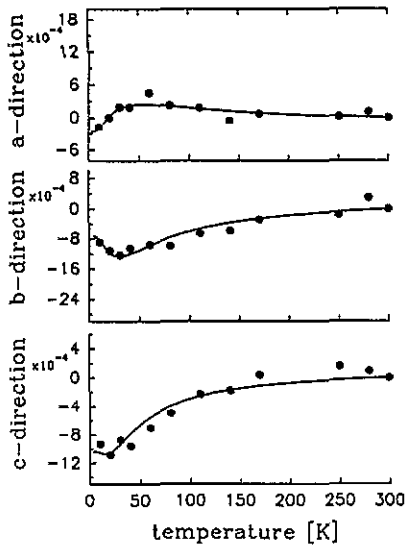

Figure 3. Experimentally determined differences of the normalized lattice parameters of $NdCu_2$ and YCu_2 (symbols). The lines represent the calculated results.

has been measured using x-ray powder diffraction. Within the paramagnetic region the anomalies in the anisotropic thermal expansion of $ErCu_2$ and $NdCu_2$ at low temperatures could be explained within the scope of the crystal-field theory. For the experimental determination of the values of $\mathbb{A}_i$ and $\mathbb{B}_i$ in equation (10) further investigations on single crystals are still necessary.

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