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# The crystal field interaction at the rare earth site in ErNiAl<sub>4</sub>

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## Abstract

Inelastic neutron scattering spectra are reported for orthorhombic ErNiAl<sub>4</sub> at temperatures ranging from 2.1 to 280 K. The neutron transitions are interpreted in terms of three reliably identified excited crystal field (CF) levels and four tentative excited levels for the  $J = 7/2$  ground term of Er<sup>3+</sup> at the single Er site. A shift in transition peak energy between 2.1 and 8.6 K is attributed to Zeeman splitting induced by magnetic order of the Er sub-lattice below  $T_N = 5.8$  K. With the aid of a suite of possible <sup>155</sup>Gd-Mössbauer spectroscopy derivations of the rank  $n = 2$  CF parameters and a simple point charge model calculation of within-rank ratios for the higher rank ( $n = 4, 6$ ) parameters, estimates are made for all nine CF parameters required for the orthorhombic C<sub>2v</sub> ( $mm$ ) Er-site symmetry.

(Some figures in this article are in colour only in the electronic version)

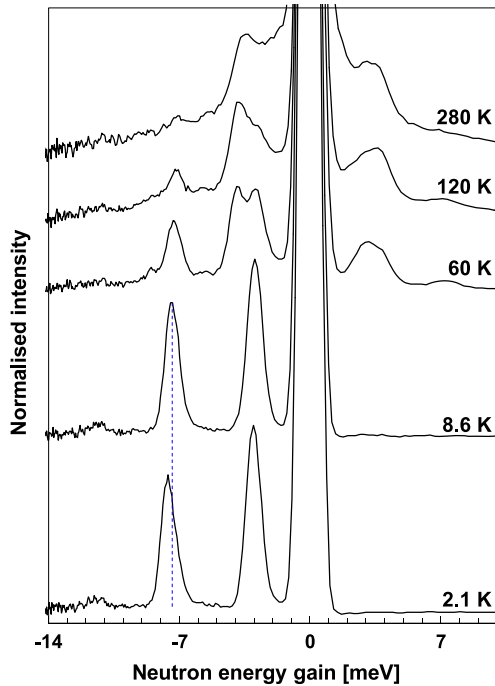
## 1. Introduction

We report here an interpretation of inelastic neutron scattering (INS) data recorded for Er<sup>3+</sup> in ErNiAl<sub>4</sub>. This work forms an important component of an ongoing, comprehensive study of the RNiAl<sub>4</sub> family of materials using a suite of techniques that includes Mössbauer spectroscopy, neutron powder diffraction, magnetometry, specific heat and electrical resistivity. The compounds investigated so far (R = Pr, Nd, Tb and Gd) exhibit antiferromagnetic order. TbNiAl<sub>4</sub> and GdNiAl<sub>4</sub> have been found to undergo at least two magnetic phase transitions as a function of decreasing temperature, including an incommensurate magnetically ordered phase [1, 2]. In the Kramers R<sup>3+</sup> cases of NdNiAl<sub>4</sub> and ErNiAl<sub>4</sub>, it is likely that the incommensurate magnetic phase persists down to very low temperatures [3]. In addition, the low temperature magnetization of TbNiAl<sub>4</sub> exhibits two transitions as a function of applied magnetic field. The orientation of the easy axis of magnetization is strongly dependent on R and it is anticipated that the other phenomena will also be influenced by the crystal field (CF) interaction at the rare earth site. Therefore it is important to characterize the CF interaction at the rare earth site for this intermetallic series.

The INS results reported here for ErNiAl<sub>4</sub> are complementary to <sup>169</sup>Tm-Mössbauer spectroscopy measurements for TmNiAl<sub>4</sub> that are currently underway and have revealed slow paramagnetic relaxation well above  $T_N \approx 5$  K. Similar behaviour has been observed elsewhere for a range of highly magnetically anisotropic hexagonal compounds (for example ErNi<sub>5</sub> [4] and TmNi<sub>5</sub> [5]). In the case of Tm compounds this indirect relaxation occurs between two singlet CF states and is not yet fully understood. Knowledge of the CF scheme is extremely important for the understanding of these relaxation processes.

## 2. Experimental details

Polycrystalline specimens of ErNiAl<sub>4</sub> and YNiAl<sub>4</sub> were prepared from high purity Er (99.9%), Y (99.9%), Ni (99.99 + %) and Al (99.99 + %) using an argon arc furnace. The specimens were prepared as sets of smaller masses (approximately 1–2.4 g), each melted at least six times to achieve good homogeneity and then annealed in vacuum at 1300 K for 7 days. All specimens were confirmed to be single phase using x-ray powder diffraction. Rietveld analyses [6]



**Figure 1.** Neutron energy loss spectra for ErNiAl<sub>4</sub> at indicated temperatures.

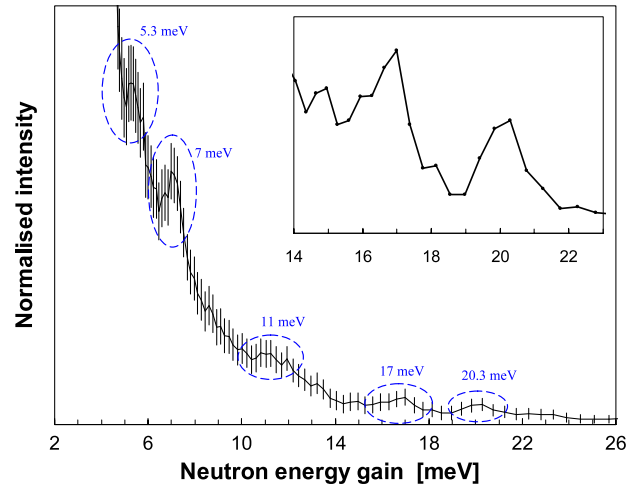
yielded average lattice parameters of  $a = 0.4037(2)$  nm,  $b = 1.5267(8)$  nm,  $c = 0.6611(2)$  nm for ErNiAl<sub>4</sub> and  $a = 0.4057(4)$  nm,  $b = 1.5382(6)$  nm,  $c = 0.6630(2)$  nm for YNiAl<sub>4</sub>, in good agreement with the values reported earlier by Rykhal *et al* [7].

The INS measurements were performed at BENSFC using the NEAT time-of-flight spectrometer (instrument V3) [8]. A 7 g mass of finely ground ErNiAl<sub>4</sub> was loaded (65% packing density) into the 50 mm diameter  $\times$  1 mm deep cavity of a rigid, aluminium holder. The sample was mounted in an ‘Orange’ helium flow cryostat at an orientation of 45° with respect to the incoming neutron beam. Since Q-dependent information was not required, the counts from all detectors (covering the range between 13° and 136°) were eventually summed. A vanadium standard sample with thickness of 1 mm was employed for the calibration of the detector efficiency and for the determination of the experimental resolution function. Neutron energy loss spectra were recorded for ErNiAl<sub>4</sub> with an incident neutron energy of  $E_i = 20.5$  meV ( $\lambda = 2$  Å, 0.5–0.8 meV energy resolution) at temperatures of 2.1, 8.6, 60, 120 and 280 K. A neutron energy gain spectrum was recorded at 280 K with  $E_i = 3.2$  meV ( $\lambda = 5.1$  Å, 0.1–0.8 meV energy resolution). Additional spectra were recorded at 280 K for the empty cell for the purpose of subtraction from the ErNiAl<sub>4</sub> spectra, and also for YNiAl<sub>4</sub> reference material (5 g, 63% packing density) to rule out the presence of phonon excitation lines.

### 3. Results and discussion

#### 3.1. Inelastic neutron scattering data

The trivalent Er<sup>3+</sup> ion is a Kramers ion with  $J = 15/2$  and, for the relatively low orthorhombic symmetry at the rare



**Figure 2.** Neutron energy gain spectrum for ErNiAl<sub>4</sub> at 280 K. The inset presents a zoomed view of the two highest energy transition peaks at 17 and 20.3 meV.

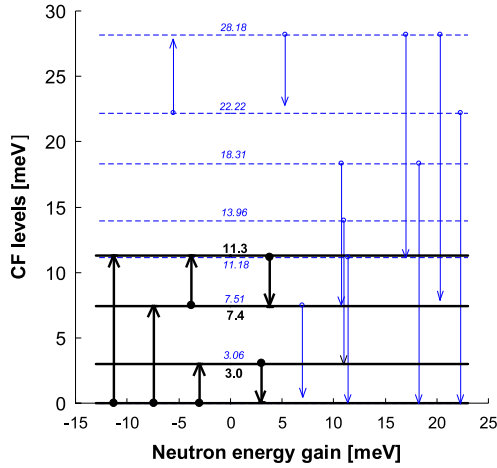
earth site, the CF scheme is comprised of 8 Kramers doublets. For ease of comparison, the neutron energy loss spectra are collected in stacked form in figure 1. At 8.6 K, only the lowest energy doublet will be populated so that the strong peaks at  $-3$  and  $-7.4$  meV and the weaker intensity peak at  $-11.4$  meV correspond to transitions to the next three excited doublets. The spectrum at 2.1 K is very similar except that the peak positions are shifted slightly. Most noticeably, the peak at  $-7.4$  meV is shifted to  $-7.6$  meV. We propose that this is brought about by Zeeman splitting of the Kramers doublets associated with the onset of antiferromagnetic order at  $T_N = 5.8$  K [3]. At 60 K, the 3 and 7.4 meV levels are significantly populated, leading to the introduction of an energy loss peak at  $-3.8$  meV (corresponding to the excitation from 7.4 to 11.3 meV) at the expense of the peak at  $-3$  meV. Energy gain peaks are also introduced at 3 and 7.4 meV. These observations are generally supported by the higher temperature spectra and there is some evidence for a further peak at about  $-5.5$  meV. The additional intensity in the  $\pm 2$  meV regions at high temperature may be due to additional low energy transitions but quasi-elastic contributions cannot be ruled out. In figure 2, the neutron energy gain spectrum is shown for ErNiAl<sub>4</sub> at 280 K. There is reasonable evidence for a low intensity peak at 7 meV and weaker intensity peaks at 5.3, 11, 17 and 20.3 meV, although the interpretation of these transitions in terms of higher energy, excited CF levels is not obvious. Based on all of these observations, we can be confident of only four CF levels, namely the ground level and the levels at excited energies of 3, 7.4 and 11.3 meV. These four levels and the relevant transitions are drawn in the CF scheme (figure 3) as bold horizontal lines and arrows, respectively.

#### 3.2. Crystal field analysis

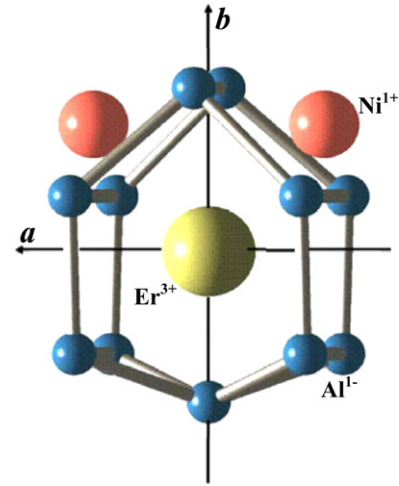
The RNiAl<sub>4</sub> series forms with the orthorhombic YNiAl<sub>4</sub>-type structure in which the R and Ni atoms each occupy single crystallographic sites [7]. As shown in figure 4, the local

**Table 1.** CF parameters fitted to the first three excited CF level energies for  $\text{Er}^{3+}$  in  $\text{ErNiAl}_4$ .  $B_2^0$  and  $B_2^2$  were fixed at possible conversions from  $^{155}\text{Gd}$ -Mössbauer data for  $\text{GdNiAl}_4$  and  $B_4^0$  and  $B_6^0$  were fitted (assuming point charge model estimates of  $r_4^2 = -3.73$ ,  $r_4^4 = -3.97$ ,  $r_6^2 = -5.06$ ,  $r_6^4 = -26.0$ ,  $r_6^6 = -29.9$  ( $r_n^m = B_n^m/B_n^0$ —refer to the text for details)).

$(x, y, z)_{\text{EFG}} \parallel$	$(z, -y, x)_{\text{CF}}$	$(y, z, x)_{\text{CF}}$	$(z, x, y)_{\text{CF}}$	$(x, -z, y)_{\text{CF}}$	$(-y, x, z)_{\text{CF}}$	$(x, y, z)_{\text{CF}}$
$B_2^0$ (K)	-0.432	-0.432	-0.199	-0.199	0.631	0.631
$B_2^2$ (K)	0.829	-0.829	-1.065	1.065	-0.233	0.233
$B_4^0$ (mK)	2.505	1.893	1.139	8.605	-5.270	-6.694
$B_6^0$ ( $\mu\text{K}$ )	23.58	17.54	19.82	19.74	15.02	-19.83



**Figure 3.** Tentative CF scheme for the  $J = 15/2$  ground state of  $\text{Er}^{3+}$  in  $\text{ErNiAl}_4$ .



**Figure 4.** Local near-neighbour environment for the  $\text{Er}^{3+}$  site in  $\text{ErNiAl}_4$ .

point symmetry at the R site is orthorhombic  $C_{2v}$  ( $mm$ ) which requires a CF Hamiltonian with nine terms:

$$\begin{aligned} \mathcal{H}_{\text{CF}} = & B_2^0 O_2^0 + B_2^2 O_2^2 + B_4^0 O_4^0 + B_4^2 O_4^2 + B_4^4 O_4^4 \\ & + B_6^0 O_6^0 + B_6^2 O_6^2 + B_6^4 O_6^4 + B_6^6 O_6^6 \end{aligned} \quad (1)$$

where we adopt the axis alignment  $(x, y, z)_{\text{CF}} \parallel (a, b, c)$ . It is unreasonable to expect that nine CF parameters can be determined when only three excited CF levels are known with confidence. For this reason, a semi-empirical approach was adopted in order to reduce the number of independent parameters that needed to be fitted.

First, the  $^{155}\text{Gd}$ -Mössbauer spectroscopy measurements reported earlier for  $\text{GdNiAl}_4$  [1] were used to estimate  $B_2^0$  and  $B_2^2$ . Given that  $\text{Gd}^{3+}$  is an S-state ion, there is no 4f shell contribution to the quadrupole splitting observed at the  $^{155}\text{Gd}$  nucleus, just the direct lattice contribution arising out of the CF. As a first approximation [9], the rank 2 CF parameters for  $\text{Er}^{3+}$  in  $\text{ErNiAl}_4$  are related to the experimentally-determined lattice electric field gradient (EFG) parameters for  $^{155}\text{Gd}$  in  $\text{GdNiAl}_4$  according to

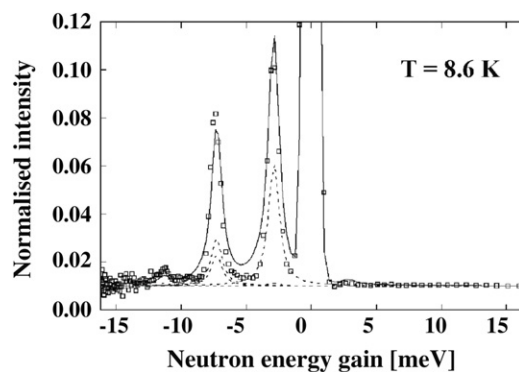
$$\begin{aligned} B_2^0 = & -\frac{e}{4}(\theta_2(1 - \sigma_2)\langle r^2 \rangle)_{\text{Er}} \left( \frac{V_{zz}}{(1 - \gamma_\infty)} \right)_{\text{Gd}} \\ \text{and} \quad B_2^2 = & \eta_{\text{Gd}} B_2^0 \end{aligned} \quad (2)$$

where  $\theta_2 = 0.0101$  and  $(1 - \sigma_2)\langle r^2 \rangle = 0.237$  au for  $\text{Er}^{3+}$  and  $(1 - \gamma_\infty)_{\text{Gd}} = 61.87$  for  $\text{Gd}^{3+}$  [10]. For orthorhombic symmetry, the principal axes of the  $^{155}\text{Gd}$ -determined EFG tensor are necessarily aligned with the crystallographic axes

but the labelling of the axes is arbitrary. Although it is convention to assume  $|V_{z'z'}| \geq |V_{y'y'}| \geq |V_{x'x'}|$  with  $0 \leq \eta'_{\text{Gd}} < 1$ , this may correspond to axes that are inconsistent with the axes adopted for the CF. For this reason, the six possible axis alignments for the reported  $^{155}\text{Gd}$ -Mössbauer values of  $V_{z'z'} = +7.98(2) \times 10^{21}$  V m $^{-2}$  and  $\eta'_{\text{Gd}} = 0.37(1)$  [1] result in six possible sets of rank 2 CF parameters for  $\text{Er}^{3+}$  in  $\text{ErNiAl}_4$ . These are listed in the first two rows of table 1.

Secondly, a simple point charge model was used to estimate the within-rank ratios,  $r_n^m = B_n^m/B_n^0$  for the ranks  $n = 4$  and 6. The calculation included only the 13 nearest neighbours (as shown in figure 4) with point charges  $\text{Er}^{3+}$ ,  $\text{Ni}^{1+}$  and  $\text{Al}^{1-}$  and the atomic position parameters due to Rykhal *et al* [7]. Taken in combination with the  $B_2^0$  and  $B_2^2$  values converted from the  $^{155}\text{Gd}$ -Mössbauer data, this meant that only the parameters  $B_4^0$  and  $B_6^0$  now needed to be fitted.

A grid search was then performed for each of the six sets of rank 2 parameters in order to determine the  $B_4^0/B_6^0$  combinations that predicted most closely the three reliable excited CF level energies determined from the INS spectra. The grid searches were extended over the ranges of  $B_4^0 = -10$  to  $+10$  mK and  $B_6^0 = -100$  to  $+100$   $\mu\text{K}$ . The  $B_4^0/B_6^0$  combinations that gave the best match to the reliable energy levels are listed in the final two rows of table 1. Whereas the locations of the INS peaks depend on the energies of the CF levels, their intensities depend on transition probabilities determined by the CF levels' eigenfunctions. When the six sets of CF parameters from table 1 were used to simulate



**Figure 5.** INS neutron energy loss spectrum for ErNiAl<sub>4</sub>. The solid theory curve represents the spectrum simulated using the CF parameters from the last column of table 1.

the 8.6 K INS spectrum, only the set from the sixth column, corresponding to  $(x, y, z)_{\text{EFG}} \parallel (x, y, z)_{\text{CF}}$ , provided a close description (figure 5). This means that the <sup>155</sup>Gd EFG axes from the earlier work were aligned with the crystallographic axes. The full CF scheme prediction based on this set of CF parameters is included in figure 3 as thin, horizontal, broken lines. At least from an energy point of view, it is possible to suggest matches with transitions in this scheme for most of the low intensity INS peaks from figures 1 and 2. For example, the peaks at  $\approx \pm 5.5$  meV could be associated with a transition between the 28.18 and 22.22 meV levels, the peaks in the vicinity of 11 meV with transitions from 18.31 to 7.51, 13.96 to 3.06 and 11.18 to 0 meV, and the peaks at  $\approx 17$  and 20.3 meV with transitions from 28.18 to 11.18 meV and 28.18 to 7.51 meV respectively. These tentative assignments are included in figure 3 as thin vertical arrows whose lengths represent the actual experimentally-determined energies of the transitions.

There are limitations to the approach that we have employed to characterize the CF interaction for ErNiAl<sub>4</sub>. The relationship between the <sup>155</sup>Gd EFG and the rank 2 CF parameters can be compromised in metallic compounds where there is increased overlap of the 4f and outer valence shells [11]. Based on their Mössbauer spectroscopy investigations of the ErNi<sub>5</sub> intermetallic series, Gubbens and van der Kraan [4] proposed that the value of  $(1 - \gamma_{\infty})_{\text{Gd}} / (1 - \sigma_2)_{\text{Er}} \approx 270 \pm 30$  is more appropriate than the theoretical value of 162 that has been employed here. The point charge model estimation of higher rank, within-rank CF parameter ratios is generally most successful for poorly conducting compounds where only a single ligand type is involved (such as oxygen ligands in rare earth based ceramic compounds). Under those circumstances, the short-range, point charge calculations approximate the superposition model [12]. Nevertheless, this work presents a valuable preliminary characterization of the full CF interaction for the heavy rare earth ErNiAl<sub>4</sub> member of the RNiAl<sub>4</sub> series and provides a platform from which to launch future refinements. In particular, it reveals that the neutron energy loss spectrum, with an effective, incident beam energy of

$\approx 15$  meV, straddles only three of the seven possible excited CF energy levels and points to the neutron beam energy that is required. Further measurements are planned with an incident neutron beam energy of 35 meV.

#### 4. Conclusion

With the aid of <sup>155</sup>Gd-Mössbauer results reported elsewhere for isostructural GdNiAl<sub>4</sub> and simple point charge model calculations, new INS spectra have been analysed to arrive at a preliminary CF characterization for the Er<sup>3+</sup> site in the heavy rare earth intermetallic, ErNiAl<sub>4</sub>. In the course of this work, the antiferromagnetic transition for ErNiAl<sub>4</sub> has been confirmed to lie between 2.1 and 8.6 K and the principal axes for the EFG tensor acting at the <sup>155</sup>Gd nuclei in GdNiAl<sub>4</sub> have been determined to align with the crystallographic axes according to  $(x, y, z)_{\text{EFG}} \parallel (a, b, c)$ . The INS spectra yielded well-defined energies for the first four Kramers doublets of the CF scheme and the preliminary CF Hamiltonian predicts the likely energies for the remaining four, with an overall CF splitting of approximately 28 meV. On the basis of this, further INS measurements are planned with the incident neutron beam energy of 35 meV.

#### Acknowledgments

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# Corrigendum

## The crystal field interaction at the rare earth site in ErNiAl<sub>4</sub>

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The authors sincerely thank Cz Rudowicz for identifying incorrect heading assignments for three of the columns in table 1. After equation (2), there is also a value of 0.0101 attributed to  $\theta_2$ . This should be changed to 0.00254. Neither of these typographical errors influenced the final outcomes, which were arrived at for the correct headings and the correct  $\theta_2$  value. However, the authors have since noticed a further, more significant error whereby equation (2) was applied incorrectly to yield  $B_2^0$  and  $B_2^2$  values of the wrong sign. The corrected signs of  $B_2^0$  and  $B_2^2$  and the corresponding  $B_4^0$  and  $B_6^0$  values that resulted from new grid searches are now listed below in a corrected version of table 1. When these six revised sets of crystal field (CF) parameters are used to simulate the 8.6 K inelastic neutron scattering (INS) spectrum, it is now the set corresponding to  $(x, y, z)_{\text{EFG}} \parallel (x, -z, y)_{\text{CF}}$  that provides a close description of similar quality to that of the existing figure 5. It is interesting that this new set of CF parameters is broadly similar in sign and magnitude to that reported in the existing publication. Another outcome is that the overall splitting of the tentative CF scheme predicted for the  $J = 15/2$  ground state of Er<sup>3+</sup> in ErNiAl<sub>4</sub> is increased from  $\approx 28$  meV to  $\approx 40$  meV. The exact arrangement of the upper levels of the CF scheme will be determined only when further INS spectra are recorded with increased incident neutron beam energy.

**Table 1.** CF parameters fitted to the first three excited CF level energies for Er<sup>3+</sup> in ErNiAl<sub>4</sub>.  $B_2^0$  and  $B_2^2$  were fixed at possible conversions from <sup>155</sup>Gd-Mössbauer data for GdNiAl<sub>4</sub> and  $B_4^0$  and  $B_6^0$  were fitted (assuming point charge model estimates of  $r_4^2 = -3.73$ ,  $r_4^4 = -3.97$ ,  $r_6^2 = -5.06$ ,  $r_6^4 = -26.0$ ,  $r_6^6 = -29.9$  ( $r_n^m = B_n^m/B_n^0$ —refer to the text for details)).

	$(x, y, z)_{\text{EFG}} \parallel$	$(y, z, x)_{\text{CF}}$	$(x, -z, y)_{\text{CF}}$	$(z, x, y)_{\text{CF}}$	$(z, -y, x)_{\text{CF}}$	$(-y, x, z)_{\text{CF}}$	$(x, y, z)_{\text{CF}}$
$B_2^0$ (K)		0.432	0.432	0.199	0.199	-0.631	-0.631
$B_2^2$ (K)		-0.829	0.829	1.065	-1.065	0.233	-0.233
$B_4^0$ (mK)		-3.468	-6.830	4.884	1.098	4.758	3.286
$B_6^0$ ( $\mu$ K)		-10.44	-27.28	23.74	21.14	15.41	17.28