Atomic displacement parameters in skutterudite compounds $R_xCo_4Sb_{12}$ (R = Ca, Yb)

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Abstract

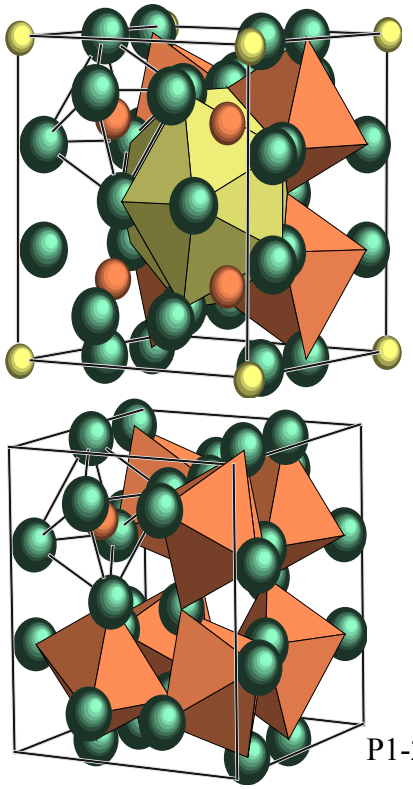
In this communication we report on powder diffraction neutron experiments performed on a series of n-type skutterudites $R_xCo_4Sb_{12}$ (R = Yb, Ca). The analyses were performed at the ISIS facility (Didcot, UK) on the POLARIS spectrometer in the temperature range 2 – 300 K. As expected, we found that the ADP values of the filler element (R atom) are much higher that those of the framework (Co and Sb). From the temperature dependence of the ADP values of the atoms, we extracted the Debye and the Einstein temperatures and deduced several other physical properties.

Introduction

The ideal thermoelectric material should conduct electricity like a metallic crystal and at the same time it should conduct heat like a glass [2]. Among the different families of material considered to fulfil these requirements, skutterudites have been widely investigated for more than 15 years now. In their structure, the M_4X_{12} (M = Co, Rh or Ir and X = P, As or Sb) corner-linked octahedral framework dominates the band structure and therefore the electronic transport. Extra inserted atoms R are loosely enclosed into the oversized framework cages made of X atoms (see Figure 1). These undersized atoms are supposed to move about in oversized cages in which they are trapped. This random motion should produce a large phonon scattering [3], and as a consequence the lattice contribution to the thermal conductivity should be strongly decreased.

Figure 1 : Unit cell of the skutterudite. M atoms are represented in orange and X atoms are represented in green. One can easily observe that they are forming tilted octahedrons. They also form dodecahedrons in which extra atoms , presented in yellow, could be inserted.

This concept of “rattle scattering” of phonons was first suggested by Slack [2]. To study this phenomenon, neutron



diffraction methods are very well *adaptated* and can easily lead to the determination of the ADP of each atom of the structure. The atomic displacement parameters (ADP) measures the mean-square displacement amplitude of an atom about its equilibrium position. In general, displacements are not the same in every crystallographic direction. For this reason, it is common to use U_{iso} which measures the mean-square displacement amplitude of the atom averaged over all directions. In the case of Sb which is not located on a site of cubic symmetry, the knowledge of these parameters could be of interest.

In this context we decided to realize a neutron diffraction study of several $R_xCo_4Sb_{12}$ samples in order to determine the ADP of each atom, its temperature dependence and try to deduce several other physical properties.

Preparation and analysis

$R_xCo_4Sb_{12}$ (R=Yb, Ca) samples were synthesized using a powder metallurgy technique which is described in details elsewhere [4] [5]. Among the series realized, the most highly filled samples were selected for neutron diffraction powder analyses, thus the compositions are the followings: $Yb_{0,18}Co_4Sb_{12}$, $Ca_{0,2}Co_4Sb_{12}$. A small part (~ 2 grams) of the hot pressed sample was crushed into fine powder. This powder was held in a vanadium can which was placed into a cryostat. The neutron scattering experiments were carried out at the ISIS facility - Ruterford Appelton Laboratory (Didcot, UK). Neutron powder diffraction data were collected using the POLARIS spectrometer which is particularly adapted to the localization of atoms and the determination of the thermal parameters, which can be done in several pressure and temperature conditions. The different temperature scanned were the followings : 2/4, 80, 150, 220 and 300 K. The Rietveld refinements were made using the Fullprof software [6].

Priorily to neutronic study, a careful characterization of the samples was done by XRD and EPMA. All the peaks of the X-ray diffraction patterns were indexed on a body-centered cubic lattice isotypic with $CoSb_3$ from which the lattice constant a can be derived. Some weak peaks due to elemental Sb and oxidized impurities were detected, but the ratio between the highest Sb peak and the highest skutterudite peak is less than 2-3 %. The presence of Sb secondary phase has been generally encounted in the synthesis of many skutterudite [7].

Results and discussion

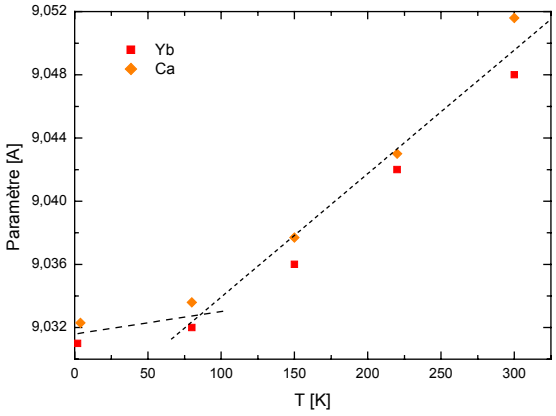


Figure 2 : Lattice constant versus temperature. The dashed line is just a guide for the eye : one can observe the linear dependency.

In Figure 2 is presented the relationship between the cell parameter determined by Rietveld method from the neutron data and the temperature for each sample. One can see that the lattice parameter increases linearly with increasing temperature, traducing the dilatation of the structure. Two different regimes are revealed by the dashed lines.

The first one stands between 0 and 75 K correspond to a very light increase of the cell parameter (~ 0,01 %). The second one appears between 75 and 300 K : the increase is there stronger and still linear. The evaluation of the slope da/dT allows us to determine the volumic thermal dilatation parameter α_T using the relation

$$\alpha_T = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P = \frac{3}{a}\left(\frac{\partial a}{\partial T}\right)_P$$

where V is the volume of the cell, a is the cell parameter and T the temperature. For

the Yb-filled sample, we find 24,5 10^{-6} K^{-1} and for the Ca-filled sample, we find 27,0 10^{-6} K^{-1}. These value are coherent with those given in the literature for $CoSb_3$ (19,1 10^{-6} K^{-1} [8]) and for n-type skutterudite partially filled with thallium (22,2 10^{-6} K^{-1} [9]).

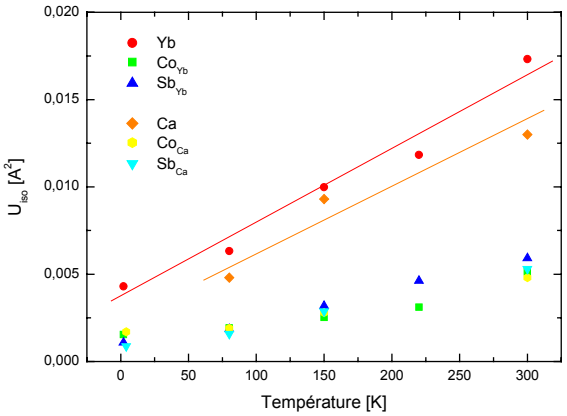


Figure 3 : Isotropic atomic displacement parameters versus temperature for $Yb_{0,18}Co_4Sb_{12}$ and $Ca_{0,2}Co_4Sb_{12}$.

The Figure 3 presents the evolution of U_{iso} versus temperature for the atoms constituting the framework Co, Sb and the filler elements Yb/Ca. One can observe that whatever the element is, U_{iso} increases linearly with temperature. This fact reflects simply the rise of the atom's displacement around its equilibrium position as the temperature increases.

One can note that the ADP of cobalt and antimony decrease to a value close to zero, which is not the case for Yb/Ca atoms. This deviation from zero is likely due to the existence of a static disorder resulting of the partial filling of the cages. This contribution should be constant with temperature [9]

At all temperatures, the values of U_{iso} for cobalt and antimony are close whatever the $R_xCo_4Sb_{12}$ compound studied. At ambient temperature, our value for Co and Sb are close to those of literature. The most striking feature is that the different inserted atoms present values of U_{iso} significantly higher than those of Co and Sb whatever the temperature is. These values illustrate the atom's tendency to oscillate around its equilibrium position ("rattling phenomenon") because of its weak bondings with the surrounding Sb atoms.

In the case of the $Yb_{0,18}Co_4Sb_{12}$ sample, several thermodynamic parameters were determined. They were deduced from the previous thermal parameters following the approach of Sales [9]. In this model, the "rattling" atoms such as the Yb are treated as localized harmonic oscillators (Einstein oscillators) and the remaining atoms (Co and Sb) as part of a Debye solid.

The adjustment of the evolution of U_{iso} with temperature for the Yb atoms allows to extract the Einstein temperature θ_E. The value of this one is determined as 70 K : this value is typical of those observed in the literature. For example, Berardan [10] identified the values of 65 K and 63 K for the compounds $Ce_{0,85}Fe_4Sb_{12}$ and $Yb_{0,92}Fe_4Sb_{12}$.

The adjustment of an average evolution of U_{iso} for Co et Sb allows to extract the Debye temperature θ_D of 280 K. Once again, these results are in well accordance with the literature : Berardan [10] found the values of 260 K and 245 K, respectively.

From θ_E and θ_D it is then possible to estimate several physical parameters like the sounds velocity and the specific heat.

From θ_D which is related to the lattice, one could extract an average sound velocity of 2672 m/s. This value agrees well with the one of 2967 m/s determined experimentally using ultrasonic transducers.

In the approach of Sales, the specific heat C can be seen as the weighted sum of the specific heat of each "part" of the material, i.e. Einstein oscillators and Debye lattice. Using this definition, we have estimated that near ambient temperature, the specific heat tends to 23,87 J/mol.atom.K, which is close to the value of 24,94 J/mol.atom.K given by the Dulong et Petit rule.

As a conclusion, neutron diffraction data confirm the large mean-square displacement of Yb and Ca in the partially filled antimonides we synthesized. The analysis of the ADPs temperature dependences have lead to the determination of several physical parameters which are in

accordance with other experimental determinations.

Acknowledgment

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