Experiment title:

Crystal structure and thermal expansion of the new high pressure *RE*$_3$Pt$_4$Ge$_{13}$ (*RE* = Pr, Sm, Eu-Yb) phases

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9

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Report:

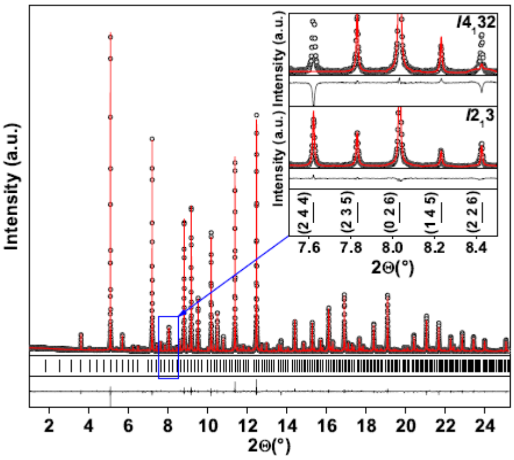

Fig. 1. Synchrotron XRD patterns (λ = 0.39987 (Å)) of Ca$_3$Pt$_{4+x}$Ge$_{13-y}$. Inset: Calculated and measured intensities in space groups $I4_132$ and $I2_13$ for reflections in the 2Θ range of 7.5-8.5°.

The experiment was devoted to a study of the crystal structure of the new high pressure *ME*$_3$Pt$_4$Ge$_{13}$ (*ME* = Ca, Y, Pr, Sm, Gd, Tb, Tm, Yb) phases and thermal expansion of YbPtGe$_2$ germanide.

The powder synchrotron X-ray diffraction (XRD) pattern of Ca$_3$Pt$_{4+x}$Ge$_{13-y}$ (161 reflections) was successfully indexed on the basis of a body-centered cubic unit cell with a lattice parameter of a = 18.0578(1) Å. Analysis of the extinction conditions showed seven possible space groups with diffraction symbols: m-3I---, m-3mI--- and $mmI4_1$--. As the first model for the refinement, the known structure of La$_3$Rh$_4$Sn$_{13}$ (space group $I4_132$, reflection conditions 00l, l = 4n) [1] was used. This refinement converged with reliability factors R_I = 0.086, R_P = 0.101 and interatomic distances, which were in good agreement with the sum of atomic radii of the elements. However, the calculated intensity of some reflections was substantially lower than the experimentally observed one (inset Fig. 1). No reasonabale structural model was found in the other six space groups with diffraction symbols mentioned above. The refinement succeeded successfully only in space group $I2_13$ as evidenced by low residuals (R_I = 0.063, R_P = 0.083) and reasonable interatomic distances.

The strongest peaks in the powder XRD pattern of the Yb$_3$Pt$_4$Ge$_{13}$ sample, measured on a HUBER G670 imaging plate Guinier camera, were indexed using a cubic primitive lattice with a_cub = 9.0045 Å (some of them are shown in Fig. 2). The presence of additional weak reflections indicated a doubling of the unit cell. Indeed, all reflections observed in the XRD pattern were indexed with lattice parameter $a \approx 2a_\mathrm{cub}$ = 18.0091 Å of a body-centered cubic lattice. However, some peaks in this pattern are either broadened or show pronounced asymmetry (Fig. 2). A clear splitting of the “broadened” and “asymmetrical” reflections is observed in high resolution (HR) synchrotron XRD experiment, thus indicating a tetragonal distortion of the lattice (Fig. 2). 122 peaks of the HR XRD pattern of Yb$_3$Pt$_4$Ge$_{13}$ were successfully indexed on the basis of a tetragonal primitive lattice with unit cell parameters a = 12.7479(1) Å, c = 9.0009(1) Å. The observed splitting pattern (e.g. (h00) reflections split into two with intensity ratio 2:1, Fig. 2) as well as the characteristic ratio of the tetragonal lattice parameters ($a_\mathrm{tetr} \approx a_\mathrm{cub}\sqrt{2}$, $c_\mathrm{tetr} \approx a_\mathrm{cub}$) corroborates a close relationship of the atomic arrangement to the cubic prototype. An analysis of the reflection conditions (l = 2n for (0kl); l = 2n for (00l)) in the HR XRD pattern of Yb$_3$Pt$_4$Ge$_{13}$ indicated 3 possible space groups: $P4_2/mcm$, $P4_2mc$ and P-42c. The reasonable structural model was found only in the non-centrosymmetric space group $P4_2mc$ (R_I = 0.061, R_P = 0.117).

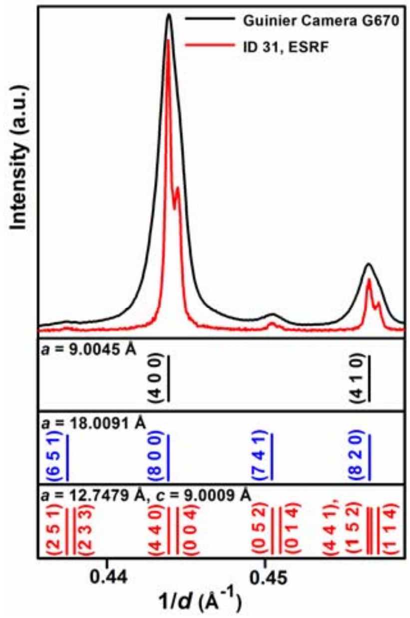

Fig. 2. Indexing of the powder XRD patterns of $Yb_3Pt_4Ge_{13}$ (see text).

Refined crystal structures of $Ca_3Pt_{4+x}Ge_{13-y}$ and $Yb_3Pt_4Ge_{13}$ allowed us to understand physical properties of these compounds, calculate their electronic structures and to explain some features of the chemical bonding in them. **These results are published in *Dalton Trans.* 41 (2012) 6299–6309.**

All peaks in the room-temperature HR-XRD pattern of $Y_3Pt_4Ge_{13}$ were successfully indexed assuming a base-centered monoclinic space group (a = 12.8781(2) Å, b = 12.8384(2) Å, c = 9.1080(1) Å, β = 90.042(2)°, V = 1505.9(1)°A3). Analysis of the reflection conditions indicated possible space groups $C2/c$ and Cc. However, the reasonable structural model was found only for space group Cc (R_I = 0.057 and R_P = 0.128) (crystal structure of $Y_3Pt_4Ge_{13}$ in space group C2/c is characterized by some disorder (two Ge atoms partially occupy their crystallographic sites) and by a strong shortening of some Ge–Ge contacts (up to 7%)). Experimental and calculated synchrotron XRD patterns as well as peaks belonging to the orthorhombic $YPtGe_2$ phase (structure type $YIrGe_2$ [3], marked by asterisks) are shown in Fig. 1. Since no overlaps of these reflections with the peaks belonging to the studied $Y_3Pt_4Ge_{13}$ compound was observed, they were excluded from the refinement. One of the peaks with weak intensity, corresponding to a monoclinic distortion of the lattice cell of $Y_3Pt_4Ge_{13}$ and indicating the true choice of the symmetry (since it cannot be indexed in the orthorhombic space groups), is presented in the inset to Fig. 3. The same structural model was confirmed for this compound at 80 K. Structural data on $Y_3Pt_4Ge_{13}$ were used as input for band-structure calculations and helped in the understanding of superconductivity appearing at T_C = 4.5 K in this high-pressure germanide. **Obtained results are submitted as a regular paper to the *Phys. Rev. B.* (2013)**

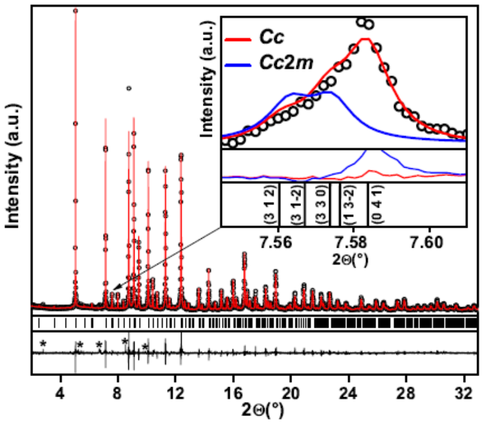

Fig. 3. Synchrotron XRD patterns (λ = 0.39987 (Å)) of $Y_3Pt_4Ge_{13}$. Inset: Calculated and measured intensities in space groups Cc and $Cc2m$ for reflections in the 2Θ range of 7.54-7.61°.

All other compounds with 3-4-13 stoichiometry containing rare-earth metals $RE_3Pt_4Ge_{13}$ (RE = Pr, Sm, Gd, Tb, Tm) were shown to crystallize with the bace-centered monoclinic $Y_3Pt_4Ge_{13}$ type. The structural relationship between $Pr_3Rh_4Sn_{13}$ prototype [2], $La_3Rh_4Sn_{13}$ type as well as discovered in the present investigation cubic $Ca_3Pt_{4+x}Ge_{13-y}$, monoclinic $Y_3Pt_4Ge_{13}$ and tetragonal $Yb_3Pt_4Ge_{13}$ types can be understood within the group-subgroup scheme and will be described in a forthcoming publication.

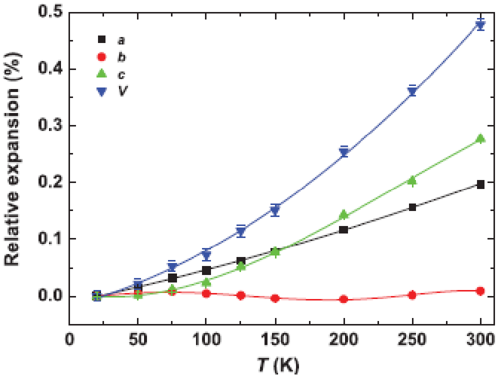

Fig. 4. Relative thermal expansion of $YbPtGe_2$. The solid lines are guide for the eyes only.

$YbPtGe_2$ is shown to crystallize with orthorombic $YIrGe_2$ type in the whole studied temperature range (20–300 K). Relative thermal expansion in all directions, which was deduced from the refinement of lattice parameters, is shown in Fig. 4. The change of lattice volume of $YbPtGe_2$ by 0.5% is typical for intermetallic compounds. However, as one can see from Fig. 4, this total thermal expansion is only due to the enlargement of the unit cell in the a and c directions. Unexpectedly, almost no expansion or even a small negative one is observed in the temperature range of 120–250 K along the b direction. A small negative volume thermal expansion is often observed for the Yb-based Kondo lattice or intermediate valence systems, but the present very anisotropic behavior is quite peculiar. **These results are published in *Phys. Rev. B* 86 (2012) 235138.**

References

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[3] M. Francois, *et al.*, *J. Less Common Met.,* 1987, **128**, 249.