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Single crystal X-ray diffraction analysis of CeCu_2Si_2

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The rare-earth copper silicide, CeCu_2Si_2 , is a heavy-fermion superconductor which was first reported by Steglich et al. [1] in 1979. An unusual type of magnetic ordering, the so-called "A-phase" [2], a superconducting "S-phase" as well as the coexistence of A- and S-phase can be observed for different crystals at temperatures $T < 1$ K. These properties depend strongly on small variations of the chemical composition. For Si-rich crystals A-phase behaviour was observed whereas the Si-deficient S-phase exhibits only superconductivity. The A/S-phase properties can be found for a composition in between. All phases are meant to crystallise within the ThCr_2Si_2 -type of structure with tetragonal space group symmetry (139) $I4/mmm$.

Three different single crystals, A-, S- and A/S-phase, were flux-grown by a modified Bridgman technique [3]. The crystals were then investigated by means of single crystal X-ray diffraction measurements at ambient conditions. Structure refinement and electron density determination of the experimental data were performed to determine the exact crystal structure and composition of the crystals.

The tetragonal structure was found for all three crystals. Significant differences were found for the unit cell parameter c which is increased for the A-phase. An unusual high electron density was found between the Si atoms which varied for the different crystals. The extinction parameter was comparably high for the S-phase crystal which supposes a very high quality crystal.

[1] Steglich, F., Aarts, J., Bredl, C. D., Lieke, W., Meschede, D., Franz, W., Schäfer, H., Phys. Rev. Lett., 1979, 1892.

[2] Stockert, O. et al. Phys. Rev. Lett., 2004, 136401-1.

[3] Jeevan, H. S. unpublished.

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Crystal structure and ferroelectricity in thiourea pyridinium salts inclusion compounds

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Bis-thiourea pyridinium salts inclusion compounds $[(\text{NH}_2)_2\text{CS}]_2\text{C}_5\text{H}_5\text{NH}^+\text{A}^-$, hereafter $\text{T}_2\text{Py}^+\text{A}^-$ where $\text{A}=\text{Cl}, \text{Br}, \text{I}, \text{NO}_3$, have been subject of intensive studies because of their interesting structural and physico-chemical properties and potential applications. They have been studied by various methods such as DSC, x-ray diffraction, proton NMR and dielectric spectroscopy [1-5]. At room temperature all halide complexes are iso-structural and crystallise in orthorhombic system, in Cmcm space group and the nitrate salt in Pbnm . In these structures thiourea molecules form hydrogen-bonded ribbons, which built parallel channels of almost squared cross section in which stacks of pyridinium cations are located. On cooling these complexes undergo one or two reversible phase transitions at different temperatures into various space groups and in the nitrate salt into a different crystallographic system:

$\text{T}_2\text{Py}^+\text{Cl}^- \text{Cmcm} \Rightarrow \text{Pbca} (a' = 2a)$

$\text{T}_2\text{Py}^+\text{Br}^- \text{Cmcm} \Rightarrow \text{Cmc}2_1 (a' = 3a) \Rightarrow \text{P}2_1\text{cn}$

$\text{T}_2\text{Py}^+\text{I}^- \text{Cmcm} \Rightarrow \text{C}2\text{cm} \Rightarrow \text{P}2_1\text{cn}$

$\text{T}_2\text{MePy}^+\text{I}^- \text{Cmcm} \Rightarrow \text{Pbcn} (c' = 3c)$

$\text{T}_2\text{Py}^+\text{NO}_3^- \text{Pbnm} (a' = 2a) \Rightarrow \text{P}2_1/c \Rightarrow \text{P}2_1$

Although the phase transitions are mainly of the second order with small structural changes only two out of five of these inclusion complexes, $\text{T}_2\text{Py}^+\text{I}^-$ and $\text{T}_2\text{Py}^+\text{NO}_3^-$ exhibit ferroelectric ordering at low temperatures. The mechanism of phase transitions and correlation between the structure, the type of an anion and N-methylation of the pyridinium and the ferroelectric properties of these new thiourea pyridinium salts will be discussed.

[1] K. Prout et al., Variable-temperature studies of order/disorder transitions in thiourea pyridinium halide crystals by XRD and solid-state ^2H NMR, Chem. Matter. (2000), 12, 3561-3569.

[2] M.Grottel et al., ^1H NMR study of molecular motions in thiourea pyridinium halide inclusion compounds, Z.Naturforsch. (2003), 58a, 638-644.

[3] M.Grottel et al. H NMR study of molecular motions in thiourea pyridinium nitrate inclusion compounds, Z.Naturforsch. (2004) 59a, 505-509.

[4] H.Małuszyńska and P.Czarnecki, Structure, phase transitions and dielectric properties of a new inclusion compound of bis-thiourea pyridinium nitrate salt, Zeitschrift f. Kristall. (2006), 221, 218-225.

[5] A.Pajzderska et al., A study of crystal structure and molecular dynamics by XRD and ^1H NMR in bis-thiourea N-methylpyridinium iodide, Molecular Physics, (2006) accepted.