

s2.m10.p5 **Fourier Difference Analysis of HoNi₂B₂C single crystals.** T. Leisegang^a, D. C. Meyer^a, D. Souptel^b, G. Behr^b and P. Paufler^a, ^aTechnische Universität Dresden, Institut für Strukturphysik, D-01062 Dresden, Germany, ^bLeibniz-Institut für Festkörper- und Werkstoffforschung Dresden, P.O.B. 27 01 16, D-01171 Dresden, Germany. E-mail: leisegang@physik.phy.tu-dresden.de

Keywords: HoNi₂B₂C; Superconductivity; Electron density

The quaternary rare earth nickel borocarbide HoNi₂B₂C, space group (139) *I4/mmm*, exhibits superconductivity and magnetic ordering at low temperatures in the range of 4 to 9 K [1]. Cooling of HoNi₂B₂C samples lead to superconductivity at temperatures of about 8 K whereas further cooling destroys it due to antiferromagnetic ordering. Regarding the magnetic susceptibility a maximum occurs at the magnetic ordering temperature of about 5 K. This phenomenon, called re-entrant behaviour, depends strongly on their composition within the small homogeneity range and the thermal treatment of crystals after growth.

Single crystals of HoNi₂B₂C were investigated by means of single crystal diffraction methods at room temperature. Structure refinement and Fourier Difference Analysis of the collected data were performed to determine small influences of disorder. The samples were grown by a vertical floating zone melting technique with radiation heating under growth conditions similar to those described in [2]. Afterwards, the samples were annealed at different temperatures and quenched rapidly from furnace to room temperature in a water bucket. With this technique it was possible to freeze-in different thermodynamic states exhibiting varying physical properties at low temperatures.

Detailed studies of the samples revealed that vanishing superconductivity is correlated with the occurrence of diffuse electron densities at the boron and carbon sites and the partial occupation of an additional Wyckoff site 8g within the unit cell. After thermal homogenisation of the samples a decrease of these diffuse electron densities, i.e. the formation of localised distributions, was observed. The results can be explained by a stochastic displacement of the boron atoms, the only position with the free structural parameter z_B . An observed localisation of the remaining electron density in the vicinity of the Ho sites is attributed to a change of the re-entrant behaviour of the superconductive samples.

- [1] Nagarajan, R., Mazumdar, C., Hossain, Z., Dhar, S. K., Gopalakrishnan, K. V., Gupta, L. C., Godard, C., Padalia, B. D., Vijayaraghavan, R. (1994). *Phys. Rev. Lett.* **72**, 274-277.
 [2] Behr, G., Löser, W., Graw, G., Bitterlich, H., Freudenberger, J., Fink, J., Schultz, L. (1999). *J. Cryst. Growth* **198/199**, 642-648.

s2.m10.p6 **Charge density of dimeric bis(N,N-diethyldithiocarbamato)zinc by combination of 100K neutron with 20K X-ray diffraction.** Marc Messerschmidt^a, Peter Luger^a, Edward R. T. Tiekink^b and Wim Klooster^c, ^aFree University Berlin, Takustr. 6, 14195 Berlin, Germany, ^bNational University of Singapore, 117543 Singapore, Singapore, and ^cBragg Institute, Australian Nuclear Science and Technology Organisation, Menai, NSW 2234, Australia. E-mail: mcmesser@chemie.fu-berlin.de

Keywords: Charge density; High resolution x-ray diffraction; Low temperature

The conventional structure of the title compound was previously determined[1]. The dimeric complex consist of a 8-membered ring including 2 Zn atoms bridged by 2 dithiolate ligands, that are related by a inversion center to one another. Including the additional ligand the Zn atom is coordinated in a 4+1 manner having 4 short(2.34-2.45Å) and one long(2.82Å) Zn-S bonds. Therefore a heavily distorted tetrahedral coordination as found seems reasonable.

To investigate in the charge density distribution a neutron diffraction experiment at 100K as well as high resolution x-ray diffraction experiments at 20K were performed[2]. The latter were done with Mo-K α (tube) and hard synchrotron radiation(0.45Å) to minimize absorption and extinction effects. To combine both experiments the hydrogen displacement factors were scale to 20K allowing an aspherical refinement of all atoms, while hydrogen positions and ADP's were held fixed. To further substantiate the experimental findings theoretical calculations for the isolated complex were performed at HF and B3LYP level of theory.

The resulting deformation density shows a remarkable orientation of Zn density in the ligand field(see figure). The topological descriptors derived from experiment agree well with the theoretical ones.

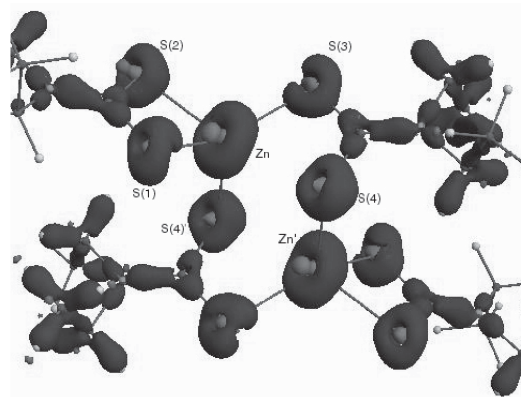


Fig. 1: deformation density isosurfaces: blue/red +/- 0.35e/Å³

- [1] Tiekink, E.R.T., *Z. Kristallogr.* - NCS **215** (2000), 445-446
 [2] Messerschmidt, M., Meyer, M., Luger, P., *J. Appl. Cryst.* (2003). **36**, 1452-1454