

Charge Density of Thermoelectric Clathrate, $\text{Na}_{8-x}\text{Rb}_x\text{Si}_{136}$

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The electronic, magnetic, spectral and conducting properties of silicon framework materials are important topics in materials research. The type I clathrate structure has been intensively investigated as part of the current search for new thermoelectric materials in materials chemistry. The more complicated type II clathrate structure has been investigated theoretically, but relatively few experimental studies have appeared. The type II structure consists of a framework forming two different cages of very different size making it possible to encapsulate cations of different sizes in the same compound. We have synthesized excellent single crystals of a type II clathrate with the composition $\text{Rb}_{7.23}\text{Na}_{16}\text{Si}_{136}$. The material has been investigated by solid state NMR on all three nuclei in the temperature range 173 K to 300 K, and by multi-temperature single crystal and powder synchrotron X-ray diffraction. Extremely extensive single crystal diffraction data ($\sin\theta/\lambda > 2 \text{ \AA}^{-1}$) were obtained at X3A1 at room temperature using a CCD detector ($a = 14.7340 \text{ \AA}$, $V = 3198.6 \text{ \AA}^3$, $V_{\text{crystal}} = 0.003 \text{ mm}^3$, $N_{\text{meas}} = 86020$, $N_{\text{unique}} = 5114$, $R(\text{int}) = 0.057$). As part of development work aiming at obtaining accurate charge densities from synchrotron X-ray diffraction data, we have for comparison also collected charge density data on our well tested conventional sequential mode Huber diffractometer in Århus ($N_{\text{meas}} = 8297$, $N_{\text{unique}} = 352$, $R(\text{int}) = 0.018$). Refinement of the combined data set gives $R_{F2} = 0.0261$ for a spherical atom model. The model shows that the large cavity is not fully occupied by Rb atoms, but it is difficult to distinguish a model with a mixture of Rb and Na atoms, and a model with partial Rb occupancy. However, solid state NMR data reveal only one Na site, and thus the structure must have partial Rb occupancy.

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