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Mapping the complete bonding network in KBH_4 using the combined power of powder diffraction and maximum entropy method

Niels Bindzus^{a,*}, Fausto Cargnoni^b, Carlo Gatti^b, Bo Richter^a, Torben R. Jensen^a, Masaki Takata^c, Bo B. Iversen^{a,*}

^a Center for Materials Crystallography, Department of Chemistry and iNANO, Aarhus University, Langelandsgade 140, Aarhus C 8000, Denmark

^b CNR-ISTM Istituto di Scienze e Tecnologie Molecolari, Via Golgi 19, 20133 Milano, Italy

^c Japan Synchrotron Radiation Research Institute, 1-1-1, Kouto, Sayo-cho, Sayo-gun, Hyogo 679-5198, Japan

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ABSTRACT

The combined power of the maximum entropy method (MEM) and synchrotron powder X-ray diffraction (SPXRD) is exerted to accurately reconstruct the electron density distribution (EDD) of the hydrogen storage material, KBH_4 . Its crystal structure features thermally activated disorder among the BH_4^- moieties, and weak secondary bonding effects occupy a key role in determining the energetic barrier for this dynamical effect. The MEM reconstruction is meticulously optimised and inspected for errors, in what may be envisaged as a general manual for this kind of studies. The successful outcome constitutes an experimental EDD of cutting-edge quality, from which atomic charges and the complete bonding network are mapped by topological descriptors. Remarkably, the chemical insights even extend to the delicate interplay of closed-shell bonding in excellent correspondence with *ab initio* and two-channel MEM calculations. For the current class of functional materials, access to such subtle electronic features is essential for the fundamental understanding of hydrogen desorption pathways.

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1. Introduction

Experimental estimation of accurate electron density distributions (EDDs) conventionally requires single-crystal diffraction data [1,2]. However, several studies have in recent years established synchrotron powder X-ray diffraction (SPXRD) as a viable alternative to probe subatomic features in highly crystalline materials [3–5]. In these instances, it outperforms single-crystal diffraction by resolving severe extinction issues, reducing absorption effects and allowing for data collection in a single exposure. The latter prevents systematic errors from merging a multitude of detector frames, each possessing a slightly different scale factor [6]. The cost of these experimental advantages is additional complications in the data analysis owing to the collapse of the three-dimensional diffraction pattern onto one-dimension. A successful outcome depends therefore critically on the process of recovering observed structure factors, F_{obs} , from the powder pattern. The premise of high-symmetry systems alleviates this inherent challenge by reducing the impact of undesirable model effects. If fulfilled, a bias-free estimation of the valence EDD is facilitated by an increased occurrence of isolated single-peaks and by a more

identifiable background profile. The recovery process may be further improved by augmenting conventional least-squares methods with advanced descriptions of anharmonic motion or chemical bonding [5,7,8].

The fundamental purpose of an X-ray diffraction experiment is to access observed structure factors, which are the Fourier coefficients of the EDD in the unit cell of the crystal. Within the branch of SPXRD, the prevailing approach for determining accurate EDDs is to regulate their Fourier inversion through the maximum entropy method (MEM) [9–11]. It eliminates the issue of unphysical series-termination ripples by inferring the most probable EDD that is compatible with the data. The concept of maximum entropy does not suffer from parameter correlation and is therefore particularly powerful in the investigation of complex structural effects, which typically occupy a key role in technologically interesting materials [12–14]. Even though the MEM yields dynamic EDDs, semi-quantitative information about chemical bonding and atomic charges may be retrieved using the quantum theory of atoms in molecules (QTAIM). The exemption is second-order derivatives, which generally experience significant dynamic perturbations [15,16]. Methodological advancements are commencing to render such subtle insights routinely available [17–19].

The present study aims at a combined experimental and theoretical characterisation of the chemical interactions in the

* Corresponding authors.

E-mail addresses: nielsb@chem.au.dk (N. Bindzus), bo@chem.au.dk (B.B. Iversen).

high-temperature phase of KBH_4 crystals using the concepts espoused in the QTAIM toolbox. Previous QTAIM investigations on hydrogen storage materials have primarily relied on theoretical calculations to identify key interactions and hydrogen desorption pathways. A notable success of this approach has been the detection of the counter-intuitive roles occupied by hydride-hydride interactions in the liberation of hydrogen from a growing number of chemical hydrides [20–24]. Hitherto, the few experimental endeavours have been compelled to probe the EDDs by SPXRD in order to properly protect the air-sensitive samples in tightly sealed capillaries. The data quality and the inherent difficulties of the subsequent data analysis restricted their outcome to the determination of atomic charges and to a qualitative mapping of the strongest chemical bonding [25–28].

At temperatures above 76 K, KBH_4 crystallises in a cubic lattice within the $Fm\bar{3}m$ (225) space group [29,30]. The peculiar feature of its crystal structure is thermally activated disorder among the BH_4^- moieties, which constantly reorient between two equally probable conformations. In consequence, the hydrogens form on average a cubic arrangement around the boron atom where each site has a 50% probability of being occupied (Fig. 1a). The family of alkaline metal borohydrides shows promise for mobile hydrogen storage owing to its high gravimetric and volumetric hydrogen content. However, future applications remain seriously limited by slow sorption kinetics and substantial dehydrogenation temperatures [31,32]. Current efforts to induce structural destabilisations and thereby enhance their hydrogen storage properties involve methods such as anion substitution and nanoconfinement [33–35]. With the exception of LiBH_4 , the alkaline metal borohydrides adopt isomorphous phases at high temperatures [36]. It is therefore essential for the entire family of compounds to explore the reorientational disorder of the BH_4^- moieties and its structural relations.

Nuclear magnetic resonance (NMR) studies corroborate that the BH_4^- anion reorients isotropically around the tetrahedral C_2 axes and that the corresponding activation energies vary non-monotonically for MBH_4 , $M=\text{Na–Cs}$ [37–39]. These observations were correlated to the strength of the single-shortest $M\cdots\text{H}$ interaction by a simplistic scheme based on the relative deviation of the actual $M\cdots\text{B}$ distance from the sum of their ionic radii. We recently elaborated on this initial hypothesis by theoretically addressing the energetic implications of reorientational disorder in the complete series of MBH_4 compounds [40]. Using a model cluster approach, the activation energies were chemically rationalised in terms of increasingly dominant destabilisation in the $M^+ - \text{BH}_4^-$ interaction, which along the alkaline series is counteracted by diminishing energy gains from relaxations in the $\text{H}\cdots\text{H}$ network. The non-monotonic departure originates from a global peak in the $M^+ - \text{BH}_4^-$ destabilisation. In a continuation of this study, we are currently employing the interacting quantum atom (IQA) approach [41] to take the chemical insights to the atomistic level and thereby reveal the atom–atom mechanisms that concur to the reorientational activation energies (manuscript in preparation).

As an augmentation to the comprehensive theoretical program exploring a variety of chemically interesting hydrogen storage materials, the present study exemplifies how to accurately probe EDDs in genuine crystal systems with the combined power of the MEM and SPXRD. We place great emphasis on the critical methodological aspects to reconstruct an EDD of cutting-edge quality for KBH_4 , which strikingly reveals the delicate interplay of closed-shell bonding transpiring among neighbouring K^+ and BH_4^- moieties. These subtle observations are validated by reconstruction of deformation EDDs and by periodic density functional theory calculations. The attained knowledge complements previous NMR and quasi-elastic neutron scattering investigations on the nature of BH_4^- reorientations and concurs to the fundamental understanding of the structural mechanisms that govern hydrogen desorption [37,39,42,43].

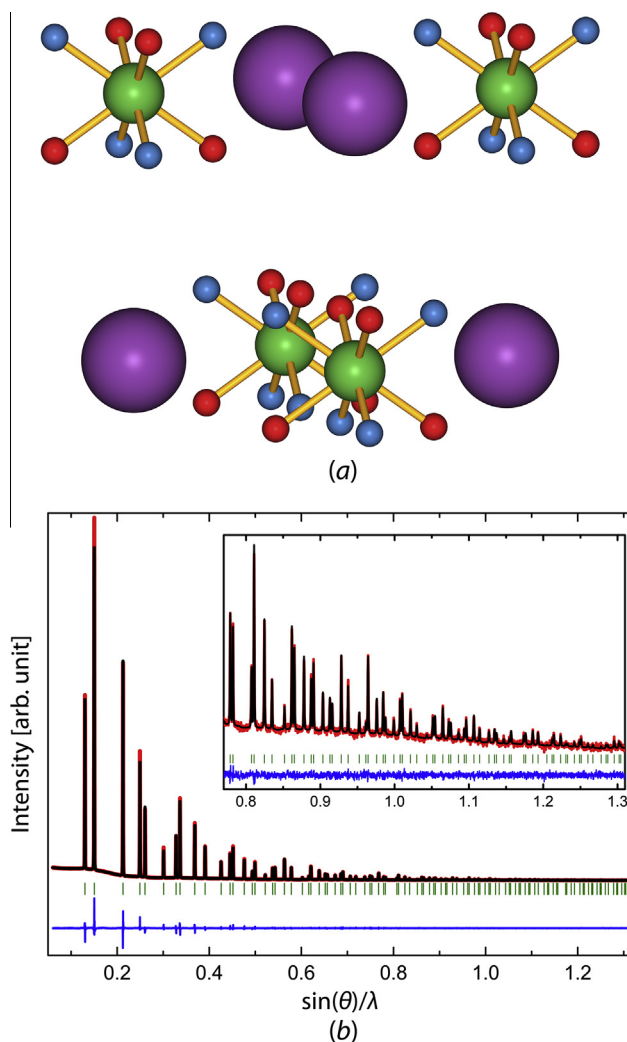


Fig. 1. (a) Crystal structure of the disordered phase adopted by KBH_4 . The two equally probable orientations of the BH_4^- moiety are emphasised by a red and blue tetrahedral arrangement of the hydrogen atoms. (b) Rietveld refinement against 100 K SPXRD data on KBH_4 . Experimental pattern (red), calculated pattern (black), difference line (blue) and location of Bragg peaks (green). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

2. Experimental and theoretical details

2.1. SPXRD experiment

High-resolution SPXRD data were collected at 100 K on a purchased powder sample of KBH_4 (Sigma–Aldrich, purity >99%) at beamline BL02B2 in the SPring-8 synchrotron facility, Japan. The white, air-sensitive powder sample was packed in a tightly sealed 0.3 mm capillary and mounted in a large image-plate Debye–Scherrer camera [44]. A radiation wavelength of $\lambda = 0.43309(2)$ Å was determined by a cerium oxide standard. Owing to the high energy of the X-ray radiation, absorption effects are negligible for KBH_4 with an angular variation below 0.1%. The temperature was controlled by a nitrogen gas flow system.

2.2. Rietveld refinement

Observed structure factors were recovered from the powder pattern by the Rietveld procedure implemented in the *FullProf* software (Table 1 and Fig. 1b) [45]. The high symmetry of the KBH_4

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