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PAPER

A combined deep inelastic neutron scattering and *ab initio* lattice dynamics study of the hydride anion dynamics and bonding in La$_2$LiHO$_3$ oxyhydride

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Abstract

Kobayashi *et al* (6279) (Science **2016**, 351) reported recently the existence of pure H$^-$ conductivity in the oxyhydride La$_{2-x-y}$Sr$_{x+y}$LiH$_{1-x+y}$O$_{3-y}$, while demonstrating its functionality through a prototype solid-state Ti/La$_2$LiHO$_3$/TiH$_2$ battery. In this study, we probe the atomistic motion of La$_2$LiHO$_3$ obtained by the promising halide salt flux method, via a combination of deep inelastic neutron scattering (DINS) and *ab initio* lattice dynamics (LD) calculations verified by vibrational inelastic neutron spectroscopy (INS). We successfully describe the measured momentum distributions from DINS via our LD calculations, without observing any diffusion activation over the temperature range reported by Kobayashi *et al.* This observation is corroborated by model predictions from our LD study, which reveals that the hydride anions remain bound within a 3D-harmonic potential. We conclude that with the current synthesis parameters, the method produces a vacancy free lattice, and that a necessary ingredient for diffusive motion of H$^-$ is the presence of a large population of vacancies. Based on the harmonic prediction for the hydrogen kinetic energy, we derive a picture of the evolution of the effective bonding potential for the hydride anions, and link this to the dynamics associated with decomposition of the oxyhydride.

1. Introduction

The oxyhydride La$_2$LiHO$_3$ has attracted significant attention since Kobayashi *et al* utilized the compound and the Sr-substituted analogues La$_{2-x-y}$Sr$_{x+y}$LiH$_{1-x+y}$O$_{3-y}$ as H$^-$-conducting electrolytes in prototype solid-state Ti/La$_2$LiHO$_3$/TiH$_2$ batteries operated at 573 K [1]. However, reading the recent literature, it become clear that there are certain ambiguities in the H$^-$-anion dynamics for this material and the need of anion vacancies.

Several methods are in use to prepare La$_2$LiHO$_3$. Both solid-state techniques (high-pressure methods or under a H$_2$-pressure) and various halide salt flux approaches that give phase pure compounds, including our recent discovery to utilize the flux below its melting temperature [1–6]. The compound normally takes an anion ordered orthorhombic Ruddlesden-Popper (RP) $n = 1$ type structure, which is described as being built of n perovskite layers (n denoting number of perovskite layers) separated by one-half rock salt layer (figure 1). Careful structural analysis by powder neutron diffraction confirms the compound to be stoichiometric without any anion vacancies, independent of the synthesis route [1, 2]. A tetragonal analogue containing anion vacancies is also reported by the high-pressure method [1].

Computationally, the migration of hydride anions in the orthorhombic La$_2$LiHO$_3$ modification is thoroughly investigated. A recent *in silico* study by Liu *et al* it was established that the migration of hydride anions in La$_2$LiHO$_3$, LaSrLiH$_2$O$_2$ and Sr$_2$LiH$_3$O took place within the perovskite layer with calculated migration energies of 0.21 to 0.45 eV [7]. Similarly, Fjellvåg *et al* connected this observation to the anisotropic ionic-
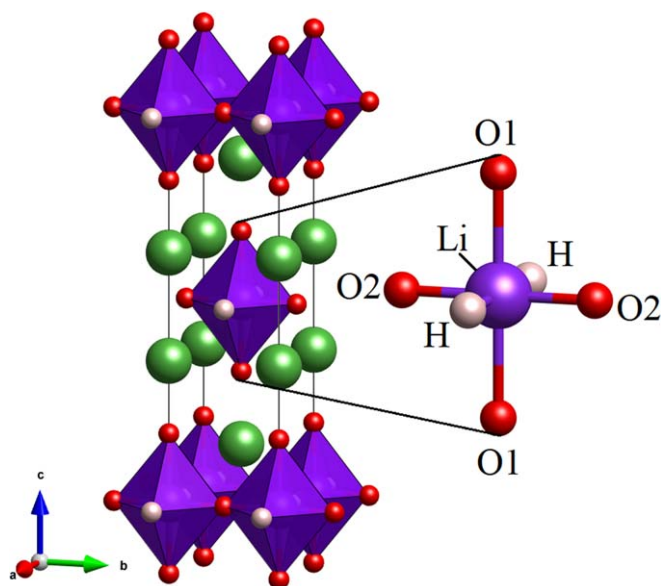
Figure 1. The Ruddlesden-Popper $n = 1$ crystal structure of orthorhombic La_2LiHO_3, built up of layers of corner-sharing LiH_2O_4 octahedra, separated by one-half LaO rock salt layer. Green, purple, white and red atoms correspond to lanthanum, lithium, hydrogen and oxygen, respectively.

covalent mixed bonding [8]. The covalent bonding in the LaO rock salt layer is effectively hindering the hydride anions to migrate into and within the rock salt layer, forcing the migration to take place in the ionic bonded perovskite layer. Furthermore, the diffusional behaviour of the anions in oxyhydrides was recently reported to be strongly correlated [9]. As the two anions types occupy the same anionic lattice, fast dynamics of both anions is a necessity to facilitate high conductivity of either specie. This observation is supported by *ab initio* molecular dynamics (AIMD) calculations stating that vacancies are needed to observe hydride anion mobility in La_2LiHO_3, $LaSrLiH_2O_2$ and Sr_2LiH_3O [10]. However, the role of vacancies is not addressed experimentally and is still unresolved.

Experimentally, the only investigations at an atomistic level on hydride anion migration in orthorhombic La_2LiHO_3 is by quasi-elastic neutron scattering (QENS) [2]. Owing to the time and space window of QENS and its inherent sensitivity to hydrogen, it is an ideal technique to study hydride anion diffusion [2, 11, 12]. For the ideal case of pure incoherent scattering, one gets direct access to the spatial self-correlation function of the H^- ions. Here, the only observed dynamics was at high temperatures (above $\sim$723 K) and associated with the decomposition of the oxyhydride, thus not the same dynamics Kobayashi *et al* observe in the prototype batteries at 573 K and in electrochemical measurements between 423 and 590 K. A possible explanation to the discrepancy between the two reports is that the hydride diffusion demonstrated by Kobayashi *et al* was outside of the dynamic window of the QENS instrument.

Spectroscopic techniques suited to study diffusional dynamics in materials such as QENS, muon spectroscopy and nuclear magnetic resonance (NMR), are limited by their spatiotemporal sensitivity windows [11–13]. In contrast, deep inelastic neutron scattering (DINS) is not limited by any time window, being in principle sensitive to all motional degrees of freedom [14, 15]. By measuring collections of recoil peaks from atomic nuclei broadened by their instantaneous momentum distributions, DINS naturally decomposes the spectra in a mass-resolved fashion. The broader the momentum distribution, the higher is the degree of bonding of a local effective potential of the mean force acting on a given atomic nucleus from its environment [14, 15]. Thereby, any subtle changes in local bonding, due to e.g. activated diffusional behaviour, can be detected. Moreover, DINS harvests absolutely all neutrons, as at very high neutron energy and momentum transfer limit (impulse approximation) the difference between the incoherent and coherent structure factor ceases to exist and the recoil peak intensities depend on the total bound (coherent and incoherent) cross section values of their respective atomic nuclei. From the material modelling point of view, DINS benefits from being in a sense the 'ultimate benchmarking tool' for the lattice dynamics (LD) calculations. Namely, it measures the amount of Doppler-broadening of atomic recoil peaks, which is proportional to atom-projected, *not total or neutron-projected*, vibrational density of states (VDOS). Hence, DINS, unlike vibrational inelastic neutron spectroscopy (INS), completely disentangles the probe (projectile, or the radiation that couples to the excitations) and the excitations themselves [14, 15]. The combination of these unique features renders DINS a well-suited technique to address the unresolved aspects of hydride anion diffusion in La_2LiHO_3.

In this work, we address the hydride anion diffusion in stoichiometric orthorhombic La_2LiHO_3 by a combination of neutron scattering techniques, theoretical models and LD calculations. DINS is used for the first time to address the unresolved aspects of dynamics and bonding in oxyhydrides. To this end, we compare the measured momentum distributions to calculated values from a LD model, and conclude on the presence of hydride anion diffusion in the compound at low temperatures. We further use INS to verify the LD calculations. By comparison between the standard deviations (SD) of nuclear momentum distributions measured and predicted based on the harmonic approximation we deduce aspects of the temperature evolution of the effective bonding strength of the hydride anions in La_2LiHO_3. Based on our findings we discuss the hydride anion diffusion in La_2LiHO_3 and address key factors for hydride anion mobility in the compound.

2. Material and methods

Phase pure powder samples of La_2LiHO_3 were synthesized in a LiCl (Sigma-Aldrich, 99.0%) flux with La_2O_3 (99.99%, Molycorp) and LiH (95%, Sigma-Aldrich) with a molar ratio of 1:4 for La_2O_3:LiH. The halide salt flux was kept at 923 K for 48 h in a calibrated tube furnace and heated and cooled with a rate of 2.5 K min^{-1}. The flux was contained in a tantalum crucible inside of an in-house built sealed stainless-steel ampule. All starting materials were dried prior to use, and the reaction mixtures and tantalum crucible were prepared inside an argon-filled MBraun glovebox. After heat treatment, the ampule was opened to air before the lithium chloride flux and excess lithium hydride were washed out with methanol (99.8%, VWR Chemicals). Because of the exothermic nature of the reaction between LiH and methanol, extra care was taken in this part of the synthesis. After washing was completed, the samples were dried under vacuum and stored inside an argon-filled glovebox.
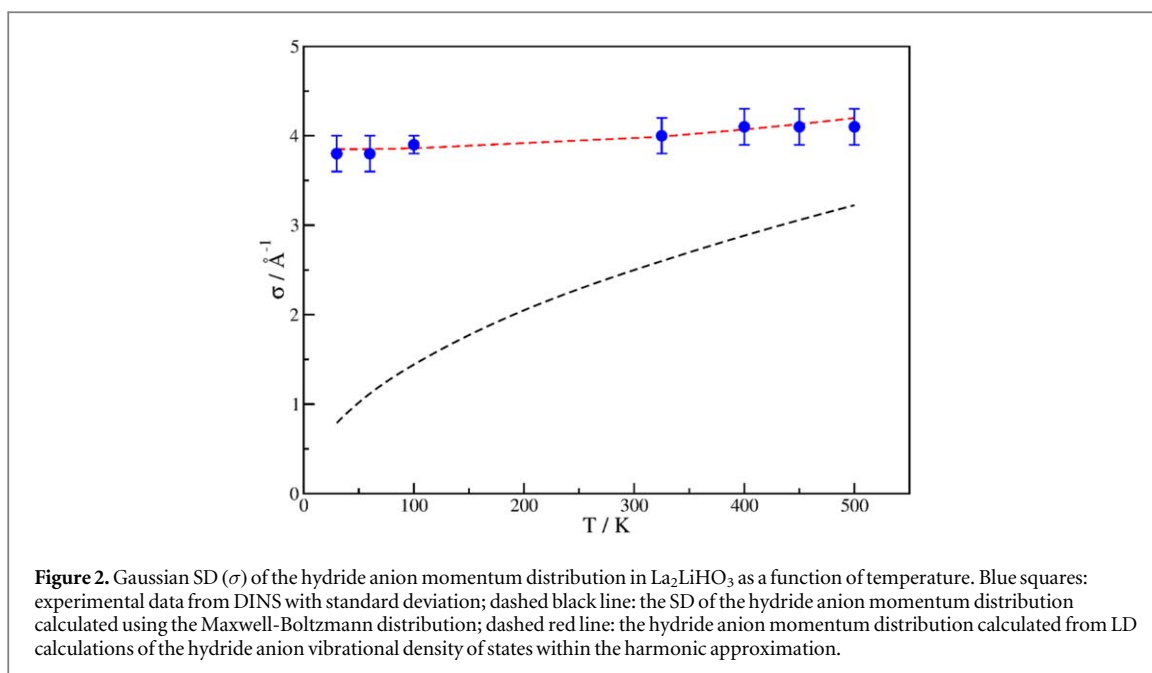
The VESUVIO spectrometer at the ISIS Pulsed Neutron and Muon source was used to carry out DINS experiments to measure the hydride anion momentum distribution in La_2LiHO_3 on a 22.7 g powder sample at a series of temperatures from 30 to 500 K, representing the range where the onset of hydride dynamics was previously reported [1, 16]. The data was corrected for sample-composition dependent gamma background and multiple scattering using newly developed routines implemented in the MantidPlot computational environment [17]. Following this, the hydrogen peaks were isolated in each spectrum recorded by an individual detector, and focused in the hydrogen longitudinal momentum space domain for increased signal-to-noise ratio and precision of the modelling of the hydride anion momentum distribution. The focused data was fitted with Gaussian hydride anion momentum distribution, and the Gaussian's SD (σ) was recorded for each temperature.

The experimental high-resolution vibrational neutron spectroscopy, INS, was carried out at the ISIS Pulsed Neutron and Muon source on the inverted-geometry TOSCA instrument at ≈ 10 K in a closed-cycle helium refrigerator [18–21]. A 5 g powder sample was measured in a flat aluminium cell with 4×4.8 cm^2 cross-section area. The software package Mantid was used for data reduction [17].

The first-principles calculations were performed based on density functional theory and the pseudo-potential method implemented in the CASTEP code [22]. Norm-conserving pseudopotentials were employed to describe the electron–ion interactions with the plane-wave cutoff energy of 850 eV. The exchange and correlation terms were described with generalized gradient approximations in the scheme of Perdew–Burke–Ernzerhof [23]. The geometric optimization of the unit cell was carried out with the Broyden–Fletcher–Goldfarb–Shanno (BFGS) minimization algorithm provided in this code. The lattice parameters and atomic positions were fully optimized using the force and stress minimization. The k-points were generated using the Monkhorst–Pack method with a grid size of $9 \times 9 \times 12$ for structural optimization. Iterative relaxation of atomic positions was stopped when the change in total energy between successive steps was less than 1 meV cell^{-1}. With this criterion, the forces generally acting on the atoms were found to be less than 10^{-3} eV Å^{-1}. Density functional perturbation theory (DFPT) [24] was used for phonon calculations. For La, Li, H, and O atoms the valence states were modelled using the $5s^2$, $5p^6$, $6s^2$, $5d^1$; $1s^2$, $2s^1$; $1s^1$; and $2s^2$, $2p^4$ electrons, respectively. The phonon calculation was weighted with the neutron scattering cross sections in the software package Mantid, thus allowing a direct comparison to the INS spectra from the TOSCA instrument [17].

3. Results and discussion

Figure 2 shows the measured and calculated (within the Maxwell-Boltzmann and the harmonic approximation) Gaussian SD for the hydrogen peak in the DINS spectra across the studied temperature range (30–500 K), corresponding to the momentum distribution of the hydride anions in La_2LiHO_3. The fact that the measured SD of the hydride anion momentum distribution strictly follow the LD prediction within the harmonic approximation across the whole temperature range is a clear signature that the only potential energy surface shape, underlying the nuclear dynamics that can be plausibly fitted to the data, given their quality, is a symmetrical harmonic potential. In such a picture, the hydride anions spend the same time on the left- and the

Figure 2. Gaussian SD (σ) of the hydride anion momentum distribution in La_2LiHO_3 as a function of temperature. Blue squares: experimental data from DINS with standard deviation; dashed black line: the SD of the hydride anion momentum distribution calculated using the Maxwell-Boltzmann distribution; dashed red line: the hydride anion momentum distribution calculated from LD calculations of the hydride anion vibrational density of states within the harmonic approximation.
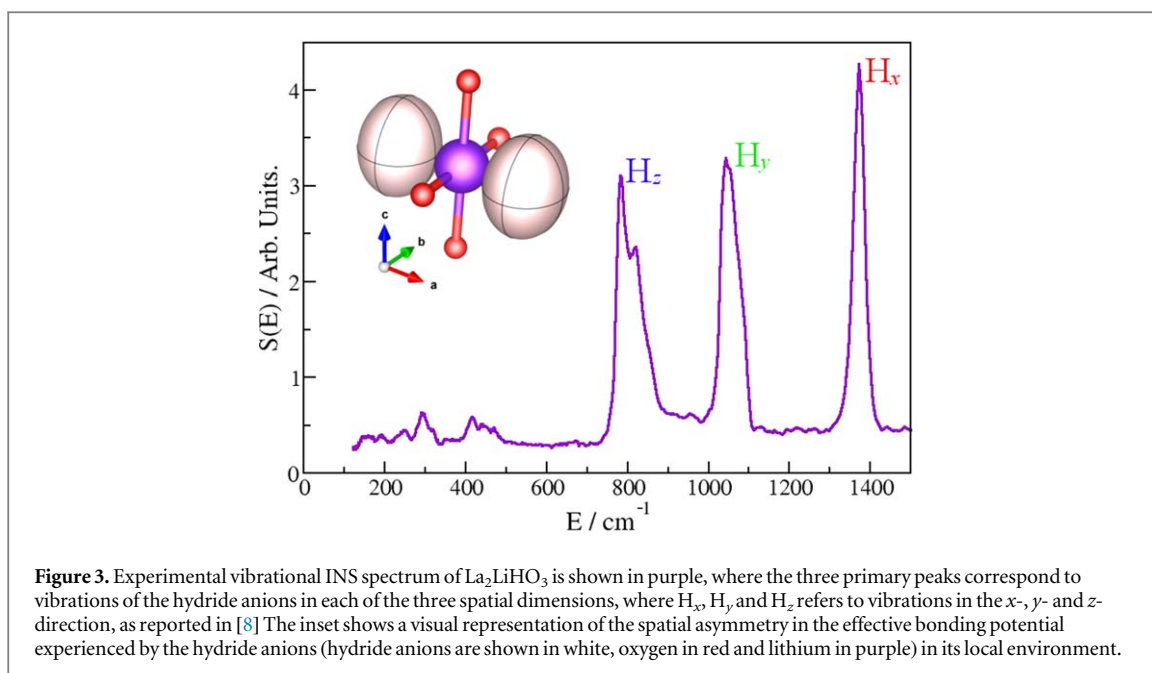
right-hand side of their local effective binding potential (as measured from the equilibrium—minimum point) and the total energy is partitioned equally between the kinetic and potential energy [14, 15, 25].

As DINS is a mass-selective, not a site-selective technique, it provides averaged-over-all-sites momentum distributions for given atomic masses. Due to the quality of the data, a fit of a combination of two nuclear momentum distributions of hydride anion, for the mobile and bound fraction, was not possible. However, had the mobile fraction of the hydride anions started to build up in the 30–500 K temperature region, the hydride anion momentum distribution, as observed by DINS, would have been observed to systematically deviate from the LD prediction. Namely, a deviation from the LD prediction would have been an indirect consequence of the failure of a single-component model to fit a two-component hydride anion momentum distribution due to a build-up of a second much narrower (and thus representing hydride anions whose kinetic energies would have been dominated by low-energy translational motion) Gaussian peak in the data. One can thus conclude that the activated diffusional behaviour of the hydride anions is not visible in this average, as the bulk of hydride anion remain tightly bonded throughout the investigated temperature range.

Although we observe no change in the shape of the local effective potential underlying the nuclear momentum distributions of the hydride anions, it does not mean that the hydride anions exhibit the same magnitude of effective bonding strength in the lattice over the whole temperature range. Unfortunately, due to the above-mentioned fact that the data quality does not support anything beyond a univariate Gaussian fit of hydride anion momentum distributions the only underlying potential of the mean force that is supported within the given data quality is harmonic. Within the infinitely-binding harmonic model, no dissociation energy is directly amenable to experimental scrutiny and thus no assessment can be made about the degree of the interplay between the localizing (binding) character of the local potential and the delocalizing character of the temperature effect on the hydride anions. However, despite this apparent lack of insight into the balance between thermal excitations and binding strength changes, one can still perform the exercise of comparing the predictions for the SD of the hydride anion momentum distributions in the completely bound hydride anions scenario, based on the lattice-dynamics simulations, with a prediction based on the model of the classical Maxwell-Boltzmann approximation of free, non-interacting particles. Such a comparison is shown in figure 2 by a black dashed line. It is evident that with increased temperature, the free-particle prediction approaches both the LD prediction and experimental values. Thus, there is a significant weakening of the effective bonding strength of the hydride anions in the lattice of La_2LiHO_3 occurring with increasing temperature as the kinetic energy of the hydride anions in La_2LiHO_3 increases while the local bonding potential is constant.

By extrapolating this trend to higher temperatures one can predict that eventually, at elevated temperatures (i.e., above 500 K limit), the effective bonding energy will be insufficient to constrain the hydride anions in their lattice sites and they will be free to migrate. In this limit we would expect increased hydride anion diffusion and can further speculate that entrance into this free diffusing regime is the origin of the thermal decomposition. This would have been observed in a DINS experiment as a significant decrease of the SD of the hydride anion momentum distribution due to the fact that the total nuclear kinetic energy of the hydride anion would have now stemmed exclusively from the low-energy translational motion, as opposed to the tightly bound hydride

Figure 3. Experimental vibrational INS spectrum of La_2LiHO_3 is shown in purple, where the three primary peaks correspond to vibrations of the hydride anions in each of the three spatial dimensions, where H_x, H_y and H_z refers to vibrations in the *x*-, *y*- and *z*-direction, as reported in [8] The inset shows a visual representation of the spatial asymmetry in the effective bonding potential experienced by the hydride anions (hydride anions are shown in white, oxygen in red and lithium in purple) in its local environment.

anion for which the bulk of the kinetic energy stems from the high-energy vibrational modes. In fact, increased hydride anion mobility at elevated temperatures is corroborated by a previous QENS study, which reported a dramatic onset of a broad QENS signal at temperatures immediately preceding the decomposition temperature (~723 K) [2]. Beyond QENS, the only way of elucidating the shape of the effective potential of the mean force using DINS data with the present level of quality is to measure a fully deuterated counterpart of the system and to resort to the mathematical relations connecting the magnitude of the isotope effect for the nuclear kinetic energy to the shape of the potential [26]. In doing so, effectively one gets 'potential selection rules' at each given temperature at which the momentum distributions could be measured for both hydrogenated and deuterated variants of the same system. In such a protocol, in principle one could fit both the dissociation energy and the decay constant parameters of the Morse potential to the observed magnitudes of the isotope effect and to infer the dissociation energy, a prospect well worthy of a future DINS experiment.

The DINS validation of the *ab initio* LD calculations, performed within the harmonic approximation, is further corroborated by comparison to vibrational INS spectrum from the INS spectrometer TOSCA, as shown in figure 3 [8]. Namely, we observe three very distinct spectral peaks which correspond to independent hydride anion motions in each of the spatial dimensions (*x*-, *y*- and *z*-direction indicated by H_x, H_y and H_z respectively in figure 3), showing that the hydride anions are situated in a 3D-multivariate harmonic potential. It is exactly the site-average of such a potential that yields the LD predictions for the mean standard deviations of hydride anion momentum distribution that are closed followed by values measured by DINS across the entire temperature range. A visual representation of the spatial asymmetry of the potential is shown in the inset of figure 3, based on the reciprocal relation between frequency and displacement within the harmonic approximation (an approximation that is corroborated by the DINS results).

The observed absence of hydride anion diffusion in La_2LiHO_3 has some implications. As we previously reported thorough structural investigations of a halide salt flux prepared La_2LiHO_3 a vacancy free lattice [2], we suggest based on our results from DINS that the absence of hydride anion diffusion is due to the lack of a large population of anion vacancies in the perovskite layer of the compound. This complies well with reported results from QENS, where no dynamical behaviour was observed in the temperature range where Kobayashi *et al* observed hydride anion diffusion [1, 2]. In addition, AIMD calculations suggest absence of hydride anion diffusion without vacancies present in the system [10]. Together, this suggests a possible discrepancy in the vacancy concentration for orthorhombic La_2LiHO_3 synthesized by the high-pressure method as this compound is reported to display hydride anion conductivity [1].

Moving forward, we would like to refine the high yield halide salt flux method by incorporating the ability to control the population of vacancies as one of the synthesis parameters. We believe this would be possible after the recent advances in preparation of oxyhydrides by the halide salt flux method [4]. We consider it feasible to synthesize e.g. $La_{2-x}Sr_xLiHO_{3-x/2}$, where the substitution level of strontium (*x*) control the vacancy concentration, thus the compound should show sufficient population of vacancies to facilitate hydride anion diffusion in the perovskite layer. Alternative other vacancy containing oxyhydrides can also be prepared by the method.

4. Summary

In this study we have employed the combination of DINS, *ab initio* LD calculations and classical models to deduce a picture of the dynamics and bonding of the hydride anions in La_2LiHO_3 over a large temperature range. Based on the success of *ab initio* LD calculations within the harmonic approximation to predict both DINS and INS result over the entire temperature range, we conclude that the hydride anions are tightly bonded in a 3D-multivariate harmonic potential throughout the studied temperature interval. Furthermore, a large vacancy population is a key to promote hydride anion diffusion in the perovskite layer of La_2LiHO_3. Our findings are supported by previous reports using QENS and AIMD [2, 10]. By comparing, across the entire temperature range, the measured SD of the hydride anion momentum distribution in La_2LiHO_3 with the prediction for free, non-interacting particles, we predict the onset of a diffusive regime close to the decomposition temperature, a phenomenon which was previously observed by QENS [2]. Furthermore, DINS, utilized here for the first time to study oxyhydrides, emerges as a powerful technique to address aspects of diffusion and bonding in complicated systems owing to the mass-selective nature of the technique.

Acknowledgments

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