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Neutron vibrational spectroscopy of imide ions (NH^{2-}) in bariumimide (BaNH)

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Abstract

Inelastic neutron scattering experiments were carried out between 20 and 4500 cm^{-1} on $Ba(NH)_{1-x}N_{2/3x}$ with $x \approx 0.1$. The concentration of defects in the structure of BaNH prevents long-range phonon coupling of the imide ions. The NH^{2-} ions in the tetragonal low-temperature phase of BaNH show a librational mode at 583 cm^{-1}, probably coupled to a translation. At 30 K the NH^{2-} ions are best regarded as statically disordered. A close comparison with the spectra of BaO and SrO was useful in the interpretation. To study the deuterium isotope shift a spectrum of the isomorphous SrND was also collected.

1. Introduction

At room temperature the imide ion (NH^{2-}) in BaNH is dynamically disordered [1]. The crystal structure has an NaCl-like arrangement, and the imide ions rotate nearly freely around their centres of mass. Cooling leads to a tetragonal phase below 192 K. In the phase transition the Ba octahedra around the NH^{2-} ions become elongated along the *c* direction. The nitrogen atoms occupy a twofold split position with a *z* parameter. The deuterium atoms are distributed over eight equivalent sites in the cubic phase. This reduces to a fourfold disorder in the tetragonal phase [1]. Figure 1 shows the imide ion surroundings at 10 K. On average half of the imide ions are oriented along the [001] direction and the other half along the [00$\bar{1}$]. The separation between the two nitrogen sites (0.48 Å) is too small to be shown in the figure.

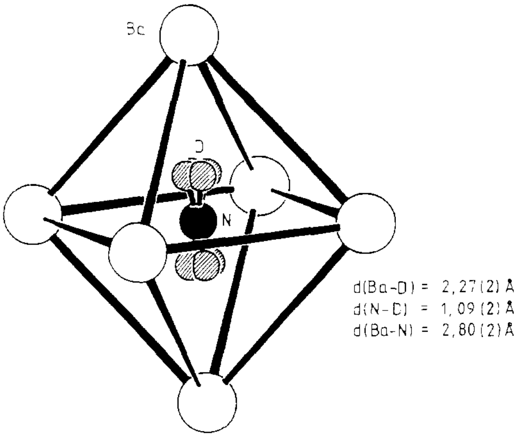

Fig. 1. The surroundings of an imide ion in BaND at 10 K.

Inelastic neutron scattering experiments on the low-temperature phase of BaNH were performed to decide between three alternative models of imide disorder. These models are: free rotational tunnelling in the solid state, dynamic disorder between fixed sites, and static disorder over fixed sites. In testing these models the compound $Ba(NH)_{1-x}N_{2/3x}$ is of greater interest than pure BaNH. This is because long-range phonon coupling between the NH^{2-} ions is suppressed.

2. Experimental details

2.1. Sample preparation

$Ba(NH_2)_2$ was prepared by the reaction of barium (Ventron, Karlsruhe, Germany, 99.5%) with liquid ammonia [2] (Messer Griesheim, Germany, 99.999%) in an autoclave [3] at 100 °C for 1 day. The amide was loaded into an MgO crucible and transferred into a glass tube connected to a Hüttig tensieudiometer [4]. After evacuation the amide was heated to 370 °C [5].

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It decomposed, evolving gaseous ammonia, according to

$$Ba(NH_2)_2 \xrightarrow{370\ °C} Ba(NH)_{1-x}N_{2/3x} + (1+x/3)NH_3 \qquad (1)$$

The volume of ammonia was measured to determine x ($x \approx 0.1$). In the interpretation of spectra isotope shifts are often useful and the preparation of BaND was considered. Unfortunately large quantities of BaND are required which cannot be prepared following eqn. (1). According to eqn. (2) we obtain for $M \equiv Sr$, pure SrND.

$$2M + N_2 + D_2 \xrightarrow{600\ °C,\ p \leqslant 100\ \text{mbar}} 2MND \qquad (2)$$

For $M \equiv Ba$ other phases appear under almost equivalent conditions (*e.g.* Ba_2ND [6]). Thus the isomorphous SrND was prepared instead of the Ba compound. This preparation is straightforward and X-ray characterization of the product is easier.

2.2. Inelastic neutron spectroscopy

The inelastic neutron scattering spectra of both compounds were obtained at 30 K on the time-focused crystal analyser (TFXA) spectrometer (at the ISIS neutron source at the Rutherford Appleton Laboratory, Chilton, UK). This spectrometer has good resolution $\Delta\hbar\omega/\hbar\omega \approx 2\%$ over the whole vibration range from 16 to 4000 cm^{-1}. The spectra were converted from detected counts *vs.* time of arrival into the conventional $S(Q, \omega)$ *vs.* energy transfer ($\hbar\omega$) according to standard programs [7]. The TFXA spectrum of 'BaNH" is shown in Fig. 2 and that of SrND in Fig. 3.

The observed band positions for both samples are summarized in Table 1. Also given in the table is the ratio ν(BaNH)/ν(SrND), which we shall take as an approximation for ν(BaNH)/ν(BaND).

3. Spectral interpretation

Because of the very small separation between the different hydrogen sites (0.5 Å) tunnelling between these sites was a real possibility. Therefore, together with Dr. M. Prager, KFA Jülich, Germany, spectra were collected at 1.5 K in the energy range 0–60 meV at the SV22, KFA Jülich, and also on IN5, ILL Grenoble These spectrometers showed no indication of tunnelling. This model can be immediately discounted.

The spectra of BaNH and SrND can be compared with the spectra of BaO [8] and SrO [9]. The atomic masses are comparable, their high-temperature structures are of the same type (NaCl), and their coordination polyhedra are also the same.

The phonon dispersion curves of SrO and the related density of states are shown in Figs. 4 and 5 respectively. The spectra are summarized, compared and approximately assigned in Table 2.

The first frequency which occurs in our BaNH spectrum with no correspondence in BaO is the NH^{2-} librational mode. The intense band at 583 cm^{-1} in the 'BaNH" spectrum has no BaO correspondence and is immediately assigned to the NH libration. Because the imide ion is linear, only two librational degrees of freedom are allowed. The 583 cm^{-1} band shows no structure and these degrees of freedom are therefore degenerate. The overtone of this mode is anticipated

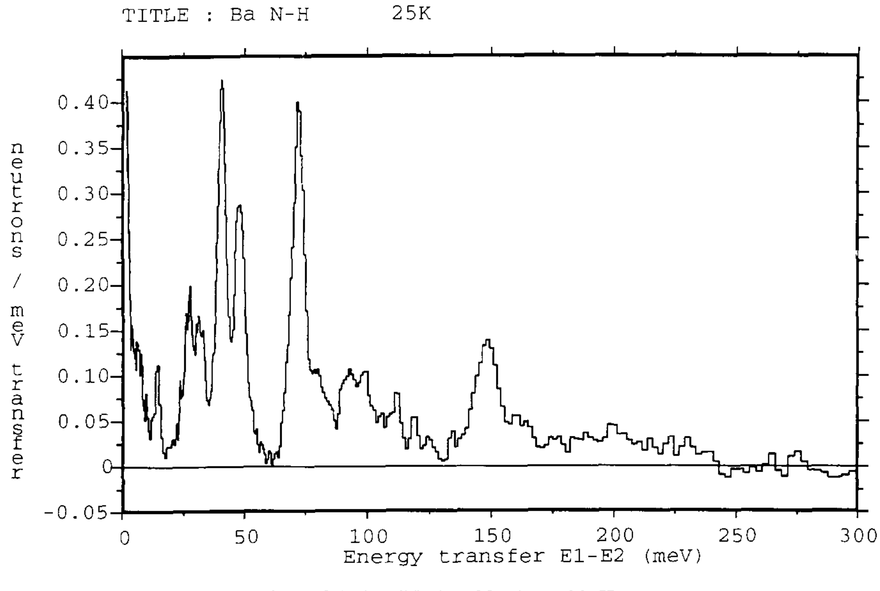

Fig. 2. TFXA spectrum of BaNH ($Ba(NH)_{1-x}N_{2/3x}$) at 30 K.

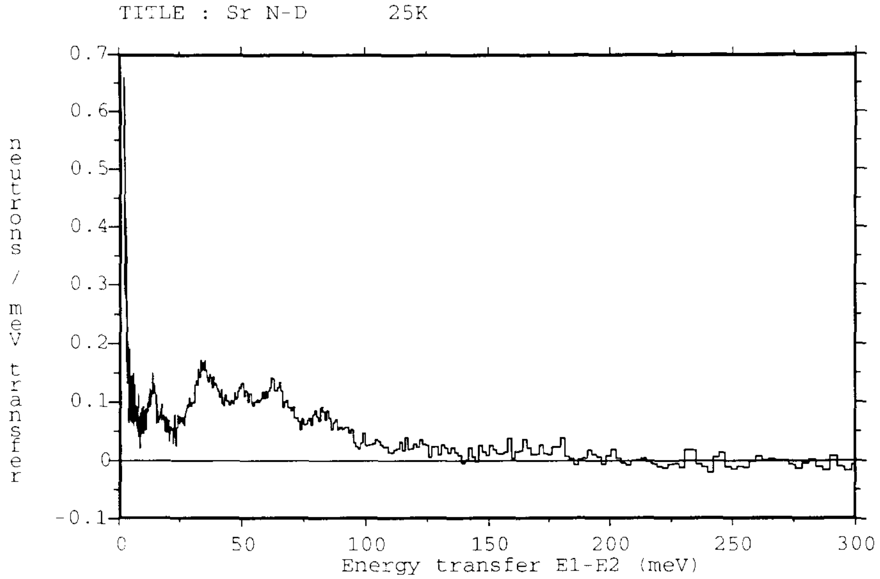

Fig. 3. TFXA spectrum of SrND at 30 K.

TABLE 1. The approximate "isotope" shift of some frequencies in BaNH/SrND

Band centre (cm^{-1}) ν(BaNH)	Band centre (cm^{-1}) ν(SrND)	Ratio ν(BaNH)/ν(SrND)
110	111	0.99
215	Superposed by next band	–
257	Superposed by next band	–
327	278	1.18
389	403	0.97
583	507	1.15

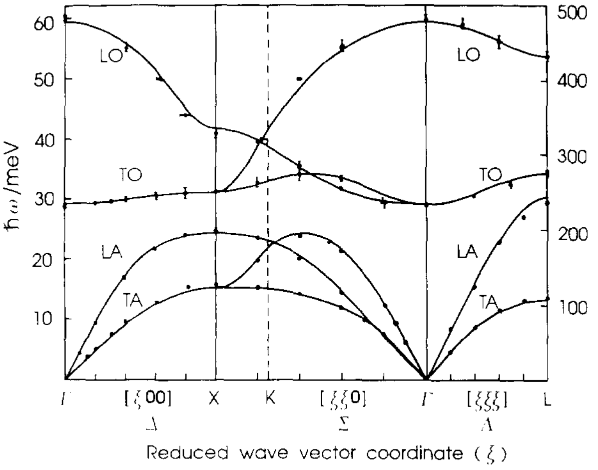

Fig. 4. Phonon dispersion in SrO [9].

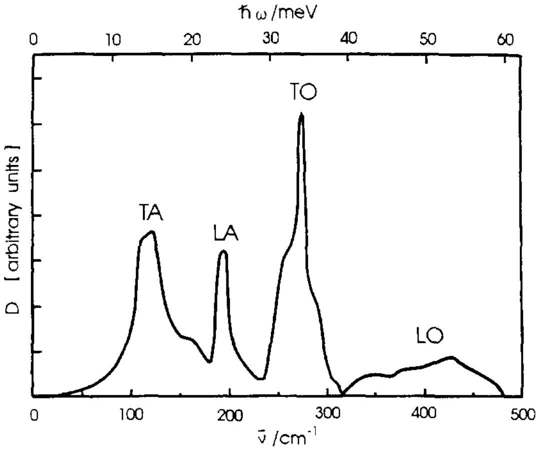

Fig. 5. Density of states in SrO [9].

at $2\times583=1166$ cm^{-1}. Indeed an appropriate band occurs at this frequency. Its intensity is only 60% of the fundamental. We deduce that the oscillator mass μm for the libration is $\mu m=1.75$ a.m.u. [10]. This will give a true isotope shift of $(2.75/1.75)^{1/2}=1.25$. The low 'isotope shift" of 1.15 in Table 1 therefore reflects a stronger librational potential in the strontium salt than in the barium salt.

Of some concern is the low intensity of the librational mode; in comparison with say, NH_4Br the translational modes are too strong and the librational mode is weak. This is mostly due to the low hydrogen atom concen-

TABLE 2. Peak positions (cm^{-1}) of the fundamentals in SrO, BaO and BaNH

Description	Peak position (cm^{-1})		
	ν(SrO)	ν(BaO)	ν(BaNH)
Transversal acoustic (TA)	100–150	60–120	110
Longitudinal acoustic (LA)	200	120–150	215–257
Transversal optic (TO)	250–300	150–230	327
Longitudinal optic (LO)	320–480	230–430	389
Libration of NH^{2-}	–	–	583

tration of imide ions compared with ammonium ions. However, this is also a reflection of the high librational oscillator mass. Some libration–translational coupling and subsequent sharing of intensity is indicated. Such coupling has been treated theoretically [11].

The comparison with NH_4^+ can be taken further. The NH_4^+ ion has an oscillator mass of $\mu \approx 4$ a.m.u. and we would expect for equivalent librational potentials that NH_4^+ librations should occur at lower frequency. This frequency would be $583(1.75/4)^{1/2} = 385$ cm^{-1}. This is much higher than the observed librational mode, at 242 cm^{-1} for NH_4^+ in $K_{0.97}(NH_4)_{0.03}Br$ [12]. Therefore the high frequency of the librational mode in the imide salts is only partly due to its light oscillator mass. We conclude that the forces between ions in this system are similar to other ionic salts but somewhat stronger.

Taken as a whole the spectrum is sharply structured and there is no evidence of structural or dynamic disorder. The imide ions are probably in well-defined deep potentials. The appearance of tetragonal site symmetry (*4/mmm*) is therefore illusory, and stems from static and statistical disorder of the imide ions about their possible sites. The true site symmetry is only *m*.

All vibrational bands observed beyond about 650 cm^{-1} are entirely due to combinations and overtones.

4. Conclusions

At 30 K imide ions in the low-temperature phase of BaNH are statically disordered. They show no rotational tunnelling. The spectra can be understood by comparison with the corresponding alkaline earth oxide spectra. The lattice vibrations (TA, LA, TO, LO) occur in the same energy regions. The NH^{2-} librational mode occurs at 583 cm^{-1}.

It would be interesting to study spectra as a function of increasing defect concentration in $Ba(NH)_{1-x}N_{2x/3}$. It may be possible to isolate an NH^{2-} ion in a matrix of "Ba_3N_2". From such measurements we would gain information about the interactions of the molecular NH^{2-} dipole anions and about the phenomenon of translation–rotation coupling in a glassy arrangement of imide ions.

Acknowledgments

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