First-Principles Lattice Dynamics Calculations of Ag⁺-Doped Alkali Halides

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The first-principles calculation method is now one of the powerful computational tools to understand the basic properties of the solid state materials, e.g., electronic structure, crystal structure, etc. Owing to the recent progresses in the computational techniques both of the hardware and the software, it has been possible to compute the full phonon dispersion of solids, which enables us to calculate the thermodynamical quantities, e.g., specific heats and vibrational entropy, as a function of temperature. A number of calculations have been already performed to investigate the structural phase transition from the Helmholtz's free energy calculations and/or the appearance of the soft mode in the phonon dispersion curves by the first-principles lattice dynamics calculations [1, 2]. However, such calculations have been carried out mainly on the perfect crystals, i.e., crystals without any defects.

In the present study, the first-principles lattice dynamics calculations for Ag⁺-doped alkali halides, the systems containing impurities, were carried out by using the direct method [1, 3]. In this method, phonon frequencies were calculated from Hellmann-Feynman (HF) forces generated by nonequivalent atomic displacement in a supercell. Here the 2×2×2 rock-salt structured supercell consisting of 64 atoms was employed, in which one of the cations in the cell was replaced by Ag⁺ for the Ag⁺-doped model. For the static calculations, the first-principles projector augmented wave (PAW) package, VASP [4, 5], was employed, in which the spin-polarized localized density approximation (LDA) [6] was used for the exchange-correlation functional. The plane wave cut off was set to 350 eV and the 2×2×2 k-point mesh was sampled in the reciprocal space by using the Monkhorst-Pack method [7]. The initial electron configurations as the valence for the PAW potential are $4d^{10}5s^1$, $2p^63s^1$, $3s^23p^64s^1$, $3s^23p^5$, $4s^24p^5$ and $5s^25p^5$ for Ag, Na, K, Cl, Br and I, respectively. Prior to giving the HF calculations with displacements of ions, the lattice parameter and the internal atomic positions were fully optimized. Then the HF forces acting on the ions of interest with small amount of displacement (δ=0.01Å) were calculated. After these static calculations, the lattice dynamics simulations were performed by the frozen phonon package, fropho [8], to compute the phonon density of states (phonon-DOS).

Calculated phonon-DOS of pure and Ag⁺-doped NaCl are shown in Fig. 1. The phonon-DOS of Ag⁺-doped NaCl is similar to that of pure NaCl, except the peak in the acoustic branch. To investigate the origin of this peak, the partial phonon-DOS was calculated. Fig. 2 shows total and partial phonon-DOSs of Ag⁺ ion and first nearest-neighboring Cl⁻ ion from Ag⁺, which suggests this peak was mainly derived from doped Ag⁺ ion.

References
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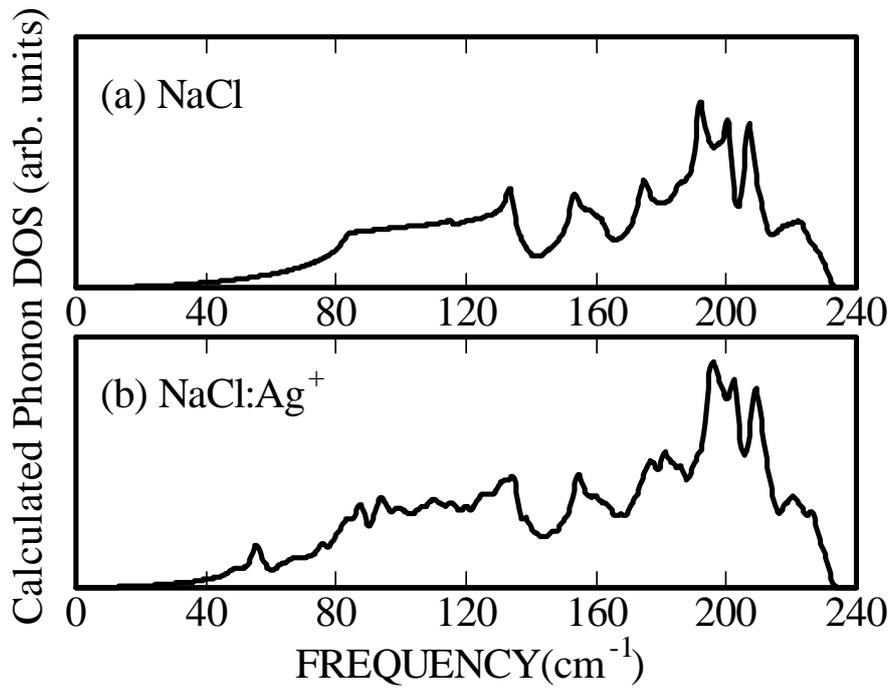*present address: Department of Materials Science and Engineering, Kyoto University

Fig. 1 Calculated phonon-DOSs of (a)NaCl and (b)Ag$^+$doped NaCl.
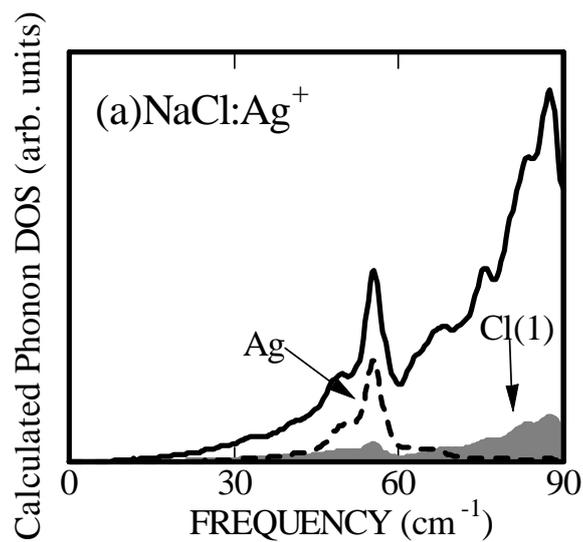

Fig. 2 Calculated total (solid line) and partial phonon-DOSs of doped-Ag$^+$(dashed line) and the first nearest neighboring (1-NN) Cl$^-$ (gray area) from doped Ag$^+$.