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Calculated surface phonon densities of states of ionic oxides and fluorides

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Abstract. Calculated phonon densities of states are reported for {0001} α -Al₂O₃, {100} SrTiO₃, {100} LiBaF₃ and {111} CaF₂.

1. Introduction

The properties of the surfaces of ionic oxides and fluorides are utilised in many technologically important areas of interest including heterogeneous catalysis, optical fibres and high-temperature superconductors. Calculated static properties such as surface crystal structure, surface energy, point defect properties and impurity segregation characteristics have been reported recently and, where it is possible to obtain a comparison, the agreement with experimental data has been encouraging [1]. Fewer calculations (and data) appear to be available for dynamic properties. This paper reports the calculated phonon densities of states of {0001} α -Al₂O₃, {100} SrTiO₃, {100} LiBaF₃ and {111} CaF₂.

2. Methods and results

An ionic description of the four materials was assumed and two-body, shell-model potentials based on electron gas theory used throughout [2]. Lattice dynamical calculations [3] were carried out for fully relaxed bulk and surface structures from which spectral densities were obtained by sampling between 1000 and 2000 points on a uniform grid in the irreducible part of the appropriate Brillouin zones. Surface-excess densities were derived from differences in the densities of states of semi-infinite slabs consisting of approximately 20 layers of ions with those of the (infinite) bulk.

All four surfaces were found to relax appreciably from bulk terminations with dilations of up to 60% and rumplings (differential cation and anion relaxation) up to 10%. The resulting surface energies were calculated to be 2.0, 1.0, 0.8 and 0.5 J m⁻² respectively for {0001} α -Al₂O₃, {100} SrTiO₃, {100} LiBaF₃ and {111} CaF₂, the corresponding unrelaxed values being 6.0, 1.8, 5.9 and 0.6 J m⁻². The calculated bulk and surface-excess densities of states are shown in figure 1. For SrTiO₃ and LiBaF₃ the surface-excess densities are for both types of surface, i.e. SrO/TiO₂ and LiF/BaF₂. Several surface-localised modes are found in each case together with decreases in

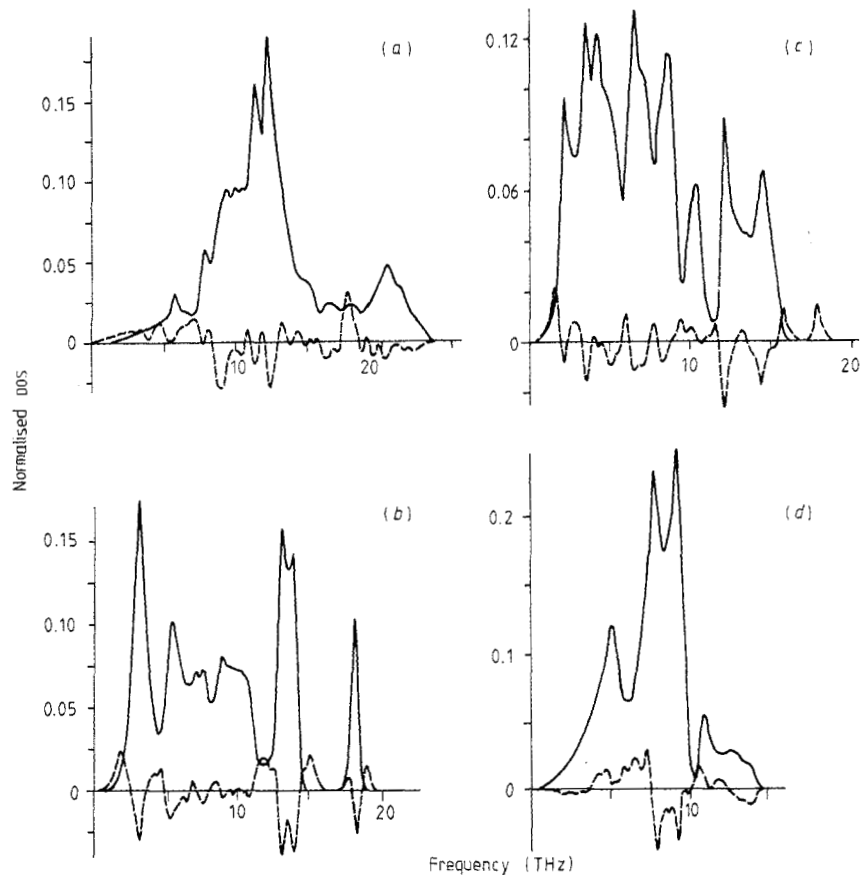


Figure 1. Calculated bulk (—) and surface-excess (....) phonon densities of states of (a) {0001} α - Al_2O_3 , (b) {100} SrTiO_3 , (c) {100} LiBaF_3 and (d) {111} CaF_2 .

intensity of important bulk modes. We note a generalised Rayleigh mode at < 2 THz in all cases and strong optic modes at ≈ 18 THz for {0001} α - Al_2O_3 , at ≈ 16 and ≈ 18 THz for {100} LiBaF_3 , at ≈ 12 THz for {111} CaF_2 and at ≈ 15.5 THz and ≈ 19.5 THz for {100} SrTiO_3 . The latter compare with the strong optic peaks reported in [4] at ≈ 14 THz and ≈ 23 THz. Of the decreases in intensity, we note, in particular, the mode at ≈ 2.5 THz in SrTiO_3 , for a comparable decrease has been found in La_2CuO_4 with the suggestion that this might be a contributory factor to the inter-granular superconducting weak links in this material [5].

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