Long-Range Coulomb Interaction in ZrO$_2$

In a recent Letter [1], Parlinski, Li, and Kawazoe reported phonon dispersion curves for cubic ZrO$_2$. Their results were obtained from first principles, using a two-step technique: (1) The interatomic force constants (IFCs) within a supercell are determined from the Hellmann-Feynman forces induced by isolated atomic displacements; (2) the dispersion curves are interpolated making the hypothesis of a finite range of all the interactions (i.e., the IFCs vanish for atoms separated by a distance exceeding the supercell size). This two-step technique had been previously applied to alkali metals [2] and monoatomic semiconductors [3]. In the present Comment, we stress it cannot be directly used for ZrO$_2$, or, more generally, for insulators with nonvanishing Born effective charges (Z^*). Consequently, the phonon band structure of Ref. [1] cannot be trusted in a large neighborhood of the Γ point.

We follow the analysis of Ref. [4]. For metals [2], the electrostatic interactions are screened for sufficiently large distances: Ignoring the effect of Friedel oscillations, seen at Kohn anomalies, the finite range hypothesis gives sensible results. For insulators, the electrostatic screening is incomplete and the range of the IFCs is driven by Coulomb interactions. In crystals with vanishing Z^*, like in most monoatomic crystals [3], the leading asymptotic term of the IFCs corresponds, at most, to a quadrupole-quadrupole interaction with typical $1/d^5$ decay (d being the distance between atoms), fast enough for the short-range hypothesis to work well. Differently, in insulators with nonvanishing Z^*, such as ZrO$_2$, the displacement of an atom creates a dipole so that the IFCs contain a dipole-dipole (DD) contribution with an average $1/d^3$ decay. The long-range character of this interaction cannot be neglected unless dramatically affecting the frequency of some long-wavelength phonons. In particular, the amplitude of the splitting between transverse (TO) and longitudinal (LO) optic modes at the Γ point [5] is driven by this interaction: Its neglect leads to a band structure without LO-TO splitting, as in Fig. 2 of Ref. [1]. The long-range character of the DD forces can be treated thanks to the knowledge of Z^* and ϵ_∞ [4,6,7]. We now report results obtained following this approach.

Our calculations were performed within the local density approximation to density functional theory. The all-electron potentials were replaced by extended norm-conserving, highly transferable pseudopotentials, with O($2s, 2p$) and Zr($4s, 4p, 4d, 5s$) levels treated as valence states. The wave functions were expanded in plane waves up to a kinetic energy cutoff of 30 Hartree. Integrals over the Brillouin zone were replaced by sums on a mesh of $4 \times 4 \times 4$ special k points [8]. We found a lattice constant of 5.02 Å, close to the experimental value of 5.09 Å [9].

We calculated Z^* and ϵ_∞ using a variational approach [7] to density functional perturbation theory. Because of
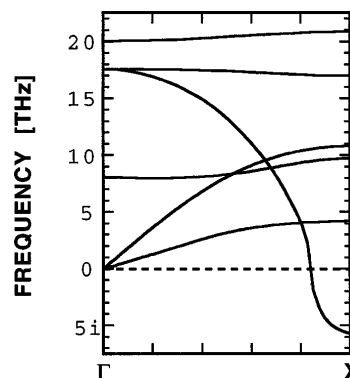

FIG. 1. Phonon dispersion curves of cubic ZrO$_2$ (Γ-X line).

the cubic symmetry, these tensors are isotropic: $Z^*_{Zr} = +5.75$, $Z^*_O = -2.86$, and $\epsilon_\infty = 5.75$. Z^*_{Zr} is anomalously large as in PbZrO$_3$ [10].

By the same technique [7], we then computed the phonon dispersion curves along the Γ-X line (Fig. 1), including correctly the DD interaction. At the Γ point, we found a triply degenerated Raman active mode of T_{2g} symmetry (17.60 THz) and a set of IR active modes of T_{1u} symmetry composed of two TO modes (8.08 THz) and a LO mode (20.07 THz). The LO-TO splitting is thus 11.99 THz, definitely not a negligible quantity. Comparing our phonon band structure to that of Ref. [1], we observe that the behavior of the LO polar branch was incorrectly described by Parlinski *et al.* The problem is particularly stringent due to the anomalously large amplitude of Z^* in ZrO$_2$.

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[1] K. Parlinski, Z. Q. Li, and Y. Kawazoe, Phys. Rev. Lett. **78**, 4063 (1997).

[2] W. Frank, C. Elsässer, and M. Fähnle, Phys. Rev. Lett. **74**, 1791 (1995).

[3] G. Kresse, J. Furthmüller, and J. Hafner, Europhys. Lett. **32**, 729 (1995).

[4] X. Gonze, J.-C. Charlier, D. C. Allan, and M. P. Teter, Phys. Rev. B **50**, 13 035 (1994).

[5] N. W. Ashcroft and N. D. Mermin, *Solid State Physics* (HRM International Editions, Philadelphia, 1976), p. 548.

[6] P. Giannozzi, S. de Gironcoli, P. Pavone, and S. Baroni, Phys. Rev. B **43**, 7231 (1991).

[7] X. Gonze and Ch. Lee, Phys. Rev. B **55**, 10 355 (1997).

[8] A $2 \times 2 \times 2$ mesh, as used in Ref. [1], was enough for ground-state properties but not for responses.

[9] G. Katz, J. Am. Ceram. Soc. **54**, 531 (1971).

[10] W. Zhong, D. King-Smith, and D. Vanderbilt, Phys. Rev. Lett. **72**, 3618 (1994).