Comment on "Why is Polonium Simple Cubic and So Highly Anisotropic?"

In a recent Letter, Legut *et al.* [1] reported that the stabilization of simple cubic (sc) structure in polonium (Po) comes from the relativistic mass-velocity and Darwin terms. Their conclusion is contradictory to our conclusion that the strong spin-orbit (SO) interaction is the origin of the stabilized sc structure in Po [2]. Legut *et al.* discussed the structural energetics based on the local-density approximation (LDA) band results, while we discussed it based on the generalized gradient approximation (GGA) [3]. In the LDA, both the semirelativistic (SR) and fully-relativistic (FR) band calculations produce the stable sc structure for Po [1]. In the GGA for Po, however, the SR band calculation yields the stable trigonal structure as for isoelectronic tellurium (Te), while the FR yields the stable sc structure [2]. Note that the SR band calculation incorporates the mass-velocity and Darwin terms only, but not the SO effect, whereas the FR considers everything.

In view of nearly the same band structures of Po and Te from the SR calculations both in the LDA and GGA, we do not think that the mass-velocity and Darwin terms are responsible for the stabilized sc structure in Po. Moreover, we are dealing with the tiny total energy difference, order of 1 meV, and so one needs the extreme precision especially in the all electron band calculation. Therefore, we rather believe that the valence band deformation induced by the strong SO interaction in Po makes the difference between Po and Te, as was proved in Ref. [2].

In the SR band scheme, the SO effect for valence bands, mainly for Po $6p$ states, is neglected. In the practical SR band calculation, the shallow Po $5d$ semicore states are treated as valence electrons, and accordingly their SO effect is neglected too. Po $5d$ orbital, however, is very localized, and so the SO effect should not be neglected to describe properly the electronic structure and the bonding property of Po. To reexamine the LDA-SR band results more carefully, we have devised the band scheme incorporating the SO effect for Po $5d$ states in the conventional SR band calculation. Since the Po $5d$ states are far separated from the valence band and the occupation for higher Po $6d$ states is nearly zero, one can separate out the Po $5d$ part in the nearly block diagonalized Hamiltonian in the l space and impose the SO effect separately. Below, we will call this relativistic band scheme as "SR-$5d$SO."

Figure 1 compares the density of states (DOS) from the SR-$5d$SO scheme with the DOSs from the SR and FR schemes. It is evident that the valence band DOSs are nearly the same between the SR and SR-$5d$SO schemes, while the SO split Po $5d$ states are nearly identical between the SR-$5d$SO and FR schemes. This figure demonstrates that the SR-$5d$SO scheme works well for the SR description of valence bands of Po.

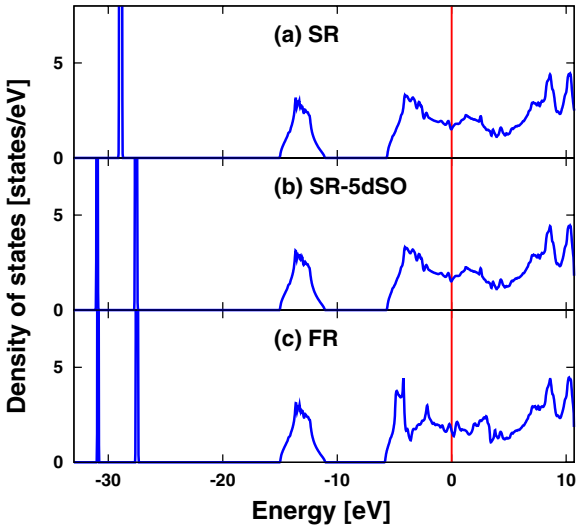

FIG. 1 (color online). Density of states from (a) the conventional semirelativistic (SR) scheme, (b) the semirelativistic scheme incorporating the SO effect of Po $5d$ (SR-$5d$SO), and (c) the fully relativistic (FR) scheme. The calculations are done for the ground state sc structure.

Quite distinctly from the conventional SR scheme [1], the SR-$5d$SO scheme yields the stable trigonal structure in the LDA, which is lower in energy than the sc structure by 1.7 meV per atom. Thus, even in the LDA, it is the SO interaction of Po $6p$ states that is responsible for the stabilized sc structure [4]. Therefore, contrarily to the claim by Legut *et al.* [1], we confirm our previous finding that the strong SO interaction is the origin of the stabilized sc structure in Po.

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[2] B. I. Min, J. H. Shim, M. S. Park, Kyoo Kim, S. K. Kwon, and S. J. Youn, Phys. Rev. B **73**, 132102 (2006).
[3] Both groups used the WIEN2K code: P. Blaha, K. Schwarz, G. K. H. Madsen, K. Kvasnicka, and J. Luitz (Karlheinz Schwarz, Technische Universitat Wien, Austria, 2001).
[4] The SR-$5d$SO scheme produces the stable trigonal Po consistently both in the LDA and the GGA.

