On the phases of Polonium

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The thermodynamical properties of the main phases of metallic polonium are examined using Density Functional Theory. The exceptional nature of the solid-solid phase transition of $\alpha$ to $\beta$ Po is underlined: it induces a lowering in symmetry, from cubic to rhombohedral, with increasing temperature. This is explained as the result of a delicate balance between relativistic and entropic effects. Overall agreement with existing experimental data is very good by state-of-the-art standards. The phonons of Po present Kohn anomalies, and it is shown that the effect of spin-orbit interactions is the inverse of that in normal metals: due to the non-spherical nature of the Fermi Surface, spin-orbit effects reduce nesting and harden most phonon frequencies.

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A frantic race is underway to find exotic new phases of elemental solids under pressure.1 With the advent of extreme diamond-anvil cell experiments with pressures beyond 1 MBar, a whole slew of new phases can be synthesized: with increasing pressure, the distance between atoms decreases, electron hybridization changes, and the nature of chemical bonds as well, changing coordination numbers and bonding directionality, orbital occupations, and so on. This is particularly dramatic in the recent demonstration that simple metals can become semiconducting if valence and core orbitals are forced to hybridize, through the application of pressure.2

Comparatively much rarer are purely temperature induced solid to solid phase transitions. Although about half of the elements present some form of solid-solid transition with $T$, most are in very limited pressure ranges, the critical pressure being more or less constant with $T$. Almost all of these transitions either increase or maintain the level of crystal symmetry (usually hexagonal to cubic, or cubic to cubic). This is intuitive, as temperature will increase inter-atomic distances, and tend to rotationally average orbital configurations, leading to high-symmetry (most often BCC) then liquid structures. The exceptions are the usual suspects: elements with complex bonding (boron, sulfur, phosphorous and bismuth), and a few of those with delicate electronic shell effects, such as Ce or Dy. In these systems, an increase in temperature can give rise to a solid phase with lower symmetry.

Polonium also falls into this category. It is one of the strangest elements of the periodic table, and the only element which adopts the simple cubic (SC) structure at ambient pressure ($\alpha$-Po, joined by a few others such as Ca-III and As-II at higher pressure). Upon increasing temperature, between 290 and 330 K, Po transforms to the $\beta$ phase, with a rhombohedral structure.

Despite its intriguing nature, experiments on Po are very difficult and rare, and little is known about its properties. Only a few laboratories in the world can synthesize Po in sufficient quantities to perform characterization. Due to their high radioactivity (with a half life of at most 100 years, depending on the isotope), samples heat and decay very quickly into Pb or Bi.

By chemical analogy, Po should behave like Se and Te, its 4p and 5p cousins, and adopt a trigonal spiral structure at low $T$. However, it was shown recently that the SC structure is stabilized over the spiral structure by relativistic effects (though there is debate over whether the scalar relativistic (SR) or spin-orbit (SO) terms dominate - see comments to Ref. 4). It was predicted that a simple rhombohedral structure would be stabilized under pressure. A qualitative explanation for the appearance of the SC structure is that the valence p states do not hybridize with $s$, because of strong relativistic repulsion of the $s$. The p states can therefore sustain purely right-angle bonding and an SC structure. Something similar probably happens in Ca and As, due to the relative (but not necessarily relativistic) changes in the s and p energy levels under pressure.

In this Letter, the vibrational and thermodynamical properties of crystalline Po are calculated from first principles. First, the effect of the spin-orbit interaction on the phonons of $\alpha$-Po is shown to be counter-intuitive, hardening phonons and reducing the nesting of the Fermi surface (FS), the opposite behavior of simple metals. Thermodynamical quantities are calculated for the low temperature phase, and agreement with experiment confirms the precision of the first principles methods. Finally, the transition temperature of Polonium is calculated at 0 pressure, comparing the Gibbs free energy of the different phases. Entropic and relativistic effects are delicately balanced and determine the stability of the $\alpha$ and $\beta$ phases as a function of temperature.

Density Functional Theory (DFT)13 and the perturbation theory built on top of it (DFPT)14 provide highly accurate calculations of the total energy and vibrational properties of materials from first principles. The implementation in the ABINIT package15 is employed,
with a plane wave basis (cut off at 435 eV) and pseudopotentials in the local density approximation [16]. Relativistic corrections are included through a pseudopotential of the HGH form [17]. The corrections are decomposed into SO and SR contributions. The calculations confirm the interpretation of Ref. [9] that the SR terms are sufficient to stabilize the simple cubic phase. Calculations without the SR relativistic terms will not be considered, because the of the structure of the pseudopotentials used, and because for heavy elements this is quite unrealistic. It is the spin-orbit term which has the largest influence on the shape of the Fermi surface (which is the central quantity affecting phonon structure). The DFPT formalism with SO is described in Refs [18, 19]. The thermodynamics of polonium are treated in the quasiharmonic approximation, fitting volume and temperature dependencies as described by Grabowski et al. [20]. The Brillouin Zone is sampled with 16\(^3\) k-points for electrons and 8\(^3\) q-points for phonons.

The α phase of polonium is simple cubic, with a lattice constant of 3.345 Å. The theoretical equilibrium lattice constant is 3.335 Å, in good agreement, and will be used in the following. The phonon band structure of Po is shown in Fig. 1 with and without the effect of the SO interaction. In a simple metal, the Fermi surface departs only slightly from a sphere. Kohn anomalies (KA) [21] appear for phonons with reciprocal space vectors \(\vec{q}\) which are nested in the surface, i.e. those \(\vec{q}\) which connect many pairs of points on the surface. These phonons are screened particularly strongly by the electrons, which renormalizes their frequency. Distorting a spherical FS, in particular because of the SO interaction, will always increase the nesting for certain \(\vec{q}\) (sometimes dramatically as in Pb [19]). In polonium, the opposite happens: due to the orbital nature and SC crystal structure, the Fermi surface is more cubic than spherical (see Fig. 2). As a result, the deformations due to the SO interaction will decrease the nesting, instead of increasing it. The small spherical hole pocket around \(\Gamma\) is also removed when the SO interaction is added. These types of effects had already been seen in other response properties in Ref. [10]. The result is quite clear in the phonon bands of Fig. 1 when including the SO interaction (going from dashed to full lines), the dips due to Kohn anomalies are reduced, and the longitudinal (LA) frequency increases. The transverse (TA) frequencies increase or decrease in different regions of the Brillouin Zone, but also present KA which are reduced by the spin-orbit interaction. From the vibrational calculations for the α phase with and without SO, it is clear that inclusion of full relativistic effects is crucial to the correct representation of the thermal properties of Po. On this basis, the thermodynamical behavior of α and β Po (and their relative stability) will be examined in the following including both SR and SO terms.

Thermodynamical quantities are calculated from the phonon bands of the bulk metal. To capture effects of thermal expansion, full phonon calculations are also performed for a volume 3\% larger than equilibrium, and the mode-dependent Grüneisen parameters are extracted (see e.g. Ref. [21] for standard formulae). The thermal expansion of Po is shown in Fig. 3 as a function of temperature; it is initially negative, which is found in many materials. For low temperatures the mode behavior near the Brillouin Zone center is crucial. The contribution from the smallest \(\vec{q}\) vectors (up to 1/8 of Brillouin Zone) is therefore fit to explicit calculations at small \(\vec{q}\) and integrated numerically.

The principal thermodynamical quantities for which there is experimental data are the thermal expansion coefficient and the heat capacity. Brocklehurst et al. [22] found a thermal expansion coefficient of \(23 \cdot 10^{-6} \pm 1.5 \cdot 10^{-6} \, ^\circ\text{C}^{-1}\) at 298 K. First principles calculations give \(16 \cdot 10^{-6} \, ^\circ\text{C}^{-1}\) which is in reasonable agreement; the residual difference is probably due to anharmonic effects.
 FIG. 3: Thermal expansion coefficient of Po as a function of temperature. Experiments\cite{22} give 23 ± 1.5 × 10⁻⁶ K⁻¹ at 300 Kelvin.

The tabulated heat capacity of polonium at 300 K is \( C_P = 26.4 \text{ J mol}^{-1} \text{ K}^{-1} \)\cite{23}, quite close to the ab initio value of 24.9 J mol⁻¹ K⁻¹ found here. The correction due to SO coupling is slight (+0.1 J mol⁻¹ K⁻¹). A fit to Murnaghan’s\cite{24} equation of state for α-Po gives a bulk modulus \( B = 39.45 \text{ GPa} \), volume 250 bohr³ and \( B' = 4.89 \).

We now turn to the thermodynamics of β-Po, and the explanation of why this lower symmetry phase is favored at higher temperatures, examining the contributions to the free energy which stabilize α or β Po at different temperatures. The beta phase of Polonium is rhombohedral, with a lattice constant of 3.359 Å and an angle of 98° 13’. It corresponds to a cube which has been slightly compressed along the (111) diagonal, and possesses fairly low symmetry. As noted in previous studies, the structure is intermediate between the SC and a body-centered-cubic phase, which is metastable at the equilibrium volume. For an angle of 60°, a face-centered-cubic phase is also metastable. For compressed volumes, calculations confirm the results of Ref.\cite{9} that a single rhombohedral phase becomes stable for volumes smaller than about 0.93\( V_0 \) (for a calculated pressure of 1 GPa), with an angle larger than 90°. Then, at compressions below 90% (for a calculated pressure between 1.5 and 2 GPa), a second phase is also stabilized, with an angle smaller than 90° (as found in Ref.\cite{9}). Fitting an equation of state to the \( E(V) \) relation gives an analytical form for the basic variation of the energy with volume. This is not simple with β-Po, for two reasons. First, phases with the equilibrium volume and unit cell angles between 90° and 100° are never even metastable with respect to α-Po. Second, fitting the equation of state to compressed rhombohedral phases is not useful, as an unrealistically large equilibrium volume is found. Given the good performance of the DFT methods for the SC phase, the experimental unit cell is used to compute the phonon bands of β-Po, and the equation of state is fit for a constant rhombohedral angle (giving \( B = 40.15 \text{ GPa} \), volume 247 bohr³ and \( B' = 4.49 \)). Thermal expansion effects are then taken into account as for the α phase. This will be a very good approximation for volumes and temperatures close to our reference point, which is the experimental volume at around 348 K\cite{6}. It has been checked that unstable modes do not appear in the various compressed or distorted structures.

The phonon band structure of β-Po is shown in Fig.\cite{4}.

 FIG. 4: The phonon band structure of β polonium along high symmetry directions of the Brillouin Zone, including the spin-orbit interaction

 FIG. 5: Free energy differences (mHa) between β and α phases of Polonium, as a function of temperature (Kelvin). Positive values favor the stability of β Polonium. Top panel: total energy at 0 K and thermally expanded volume. Middle panel: vibrational free energy at constant volume \( F_{\text{vib}} \). Bottom panel: volume-correction \( \Delta F_{\text{vib}} \) (solid), electronic free energy at constant volume \( F_{\text{el}} \) (dash), and volume-correction \( \Delta F_{\text{el}} \) (dot-dash). Differences are small below 600 K. It is the two vibrational free energy terms that determine the transition temperature from α to β Po.
along the same high-symmetry directions as in Fig. 1. (the SC nomenclature is used for simplicity). The phonons are calculated at 0 K (thermal expansion is later taken into account as for the α phase), and would change somewhat due to anharmonic effects (see e.g. Ref. [23]). Work in this direction is ongoing, but the current agreement with experiment suggests that anharmonic effects are small. It has been checked that lowering the electronic temperature does not lead to unstable phonons (in particular for the dip between L and Γ), such that the thermodynamics described by the 0 K phonons is physical. The free energy is calculated for α and β-Po, adding the ground state energy to the vibrational and electronic free energies. The free energies are calculated at a second volume V', and an additional correction is added, taking the thermal expansion into account (bottom panel of Fig. 5):

\[ \Delta F_x(T) = (F_x(V', T) - F_x(V_0, T)) \cdot (V(T) - V_0)/(V' - V_0) \]

where \( x \) is vibrational or electronic. The volume \( V \) is calculated at 0 K (thermal expansion is later taken into account as for the Po). The phonons are described by the 0 K phonons is physical. The free energy fit parameters, and does not take into account anharmonic corrections. This is in quite good agreement with experimental data which give a range of transition temperatures from 290 to 330 K. Omitting the thermal expansion or any of the free energy terms removes the transition and stabilizes α-Po for all temperatures.

In summary, this Letter presents an ab initio study of the different thermodynamical phases of crystalline Po. The effect of spin-orbit coupling on the phonon band structure of simple cubic Po is first shown to be the opposite of that on simple metals: as the initial Fermi surface (without SO) is strongly nested, the SO correction reduces the nesting and the resulting Kohn anomalies, and hardens most phonon frequencies. The inclusion of SO effects is essential to the correct representation of the phonons. Due to the delicate bonding characteristics of Po, whose low temperature simple cubic phase is stabilized by relativistic effects, increasing the temperature has the completely counter-intuitive effect of stabilizing a less symmetric phase (rhombohedral β-Po). This transition originates in the competition of relativistic stabilizing effects for the α phase and slightly more favorable vibrational entropy and thermal expansion for the β phase. A number of other elements are likely to have temperature behaviors similar to Po: either due to relativistic or pressure effects, complex bonding environments open the way for radically different symmetry breaking as a function of temperature, when entropic effects are of the same order of magnitude as the energy differences between bonding types.

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