Structural phase transitions in crystals: phonons as Higgs and Goldstone excitations

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It has recently been indicated that optical and acoustic phonons could be identified with Higgs and Goldstone excitations of the crystal lattice arising from the spontaneous breaking of a global, continuous symmetry. Here, we support this view considering structural phase transitions induced by temperature, from the face-centered-cubic (*fcc*) phase of cobalt, and from the body-centered-cubic (*bcc*) phase of zirconium and titanium, to their hexagonal-close-packet (*hcp*) phase. The Higgs field potential is identified with the Ginzburg-Landau free energy difference calculated and available in literature for the concerned structural phase transitions. In all the considered cases, the ensuing spontaneous symmetry breaking makes the optical phonon (identified with the Higgs mode) to arise only in the less symmetric *hcp* phase. This demonstrates Higgs excitations to be associated not only with quantum phase transitions, but also with structural phase transitions in natural crystals.

1 Introduction

The concept of spontaneous symmetry breaking (SSB) is well known in the Standard Model of particle physics, where the mass-generating mechanism described by P. W. Higgs[1] in 1964 removed the obstacles encountered when attempting to construct a unified gauge invariant theory of electromagnetic and weak interactions.[2]
In condensed matter physics a similar concept was formulated in somehow different, but conceptually akin way, by V. L. Ginzburg and L. D. Landau[3] in 1950, an approach that inspired P. W. Anderson[4] to describe the plasmon phenomenon in a way acknowledged by P. W. Higgs himself as a cornerstone for his own work. The latter started by writing a gauge invariant Lagrangian density that included a potential exhibiting a spontaneous breakdown of $U(1)$ (rotational) symmetry, the same path followed by Ginzburg and Landau when trying to describe superconductivity without investigating its microscopic origin. They argued that, when a system makes a phase transition from the normal to the superconducting phase, a complex order parameter ϕ emerges, and the system undergoes a SSB: its free energy density $F(\phi)$ can be expressed in the ordered phase as

$$F(\phi) = -\frac{\mu_0^2}{2}\left(\phi\phi^*\right) + \frac{\lambda}{4}\left(\phi\phi^*\right)^2 + O(|\phi|^6) \tag{1}$$

with μ_0^2 and λ real and positively defined parameters. The microscopic origin of the $U(1)$ symmetry breaking emerged only some years later, thanks to the works by J. Bardeen, L. N. Cooper and J. R. Schrieffer (BCS theory):[5,6] phonons mediate an attractive interactions among electrons, and the simplest scalar state that can be constructed from the electron pair with zero total spin is $|\psi\rangle = c^\dagger_{\mathbf{k}\uparrow}c^\dagger_{-\mathbf{k}\downarrow}|0\rangle$, where $c^\dagger_{\mathbf{k}\uparrow}$ creates from the vacuum an electron state with wavevector $\mathbf{k}$, and the arrow represents the electron spin state. The interaction term in the Hamiltonian,

$$H_{\mathrm{BCS}} \propto c^\dagger_{\mathbf{k}\uparrow}c^\dagger_{-\mathbf{k}\downarrow}c_{\mathbf{k}\uparrow}c_{-\mathbf{k}\downarrow}, \tag{2}$$

is locally gauge invariant with $U(1)$ as gauge group with parameter θ, which transforms $|\psi\rangle$ into $e^{i\theta(x)}|\psi\rangle$. However, in its mean-field approximation, the interaction term becomes $\hat{H}_{\mathrm{BCS}} \propto \Delta_{\mathbf{k}}c^\dagger_{\mathbf{k}\uparrow}c^\dagger_{-\mathbf{k}\downarrow} + \Delta^*_{\mathbf{k}}c_{\mathbf{k}\uparrow}c_{-\mathbf{k}\downarrow}$, and the continuous $U(1)$ symmetry is broken, since only the particular values $\theta = 0$ and $\theta = \pi$ make $\hat{H}_{\mathrm{BCS}}$ gauge invariant. Here $\Delta_{\mathbf{k}}$ is the energy gap of the Cooper's pair,[5,6] the superconducting phase is the ordered phase, and notably Gor'kov and Melik-Barkhudarov demonstrated[7] that a rigorous microscopic evaluation of $\hat{H}_{\mathrm{BCS}}$ provides the Ginzburg-Landau free energy expression in Equation (1), with $\Delta_{\mathbf{k}}$ as order parameter.

Equation (1) also describes other quantum phase transitions, e.g. in materials that make a transition from a paramagnetic (disordered) to a ferromagnetic (ordered) phase, when the system temperature T drops below the Curie temperature. In this case, the field ϕ – the order parameter – is the magnetization, and in the ordered phase the system chooses a particular spatial direction θ_0, along which the atomic spins result self-oriented: the system is no more $U(1)$-invariant. For these materials, the Higgs and Goldstone modes respectively correspond to the modulation of the amplitude and phase of the magnetization, the order parameter that emerges when the continuous rotational symmetry is broken.
The existence of such oscillatory modes seems pervasive. The Higgs mechanism has been acknowledged in topological insulators, Weyl semimetals, and in cuprates;[8–13] at the quantum phase transition between the superfluid and insulating phases;[14,15] at the transition from a sea of spin-singlet pairs to a long-range antiferromagnet;[16] in superconductors,[17,18] etc. Recently, the presence of structural Goldstone and Higgs modes was suggested by first-principles calculations[19] on a perovskite oxide, $SrMnO_3$, and it was demonstrated in a supersolid quantum gas.[20]
In a recent work,[21] we suggested that the *optical* and *acoustic* phonons can be identified with Higgs and Goldstone excitations of the crystal lattice arising from the spontaneous breaking of some global, continuous symmetry. Although this description has been already considered as plausible in literature,[22,23] the occurrence of Goldstone and Higgs modes in a clearly identifiable *structural* phase transition occurring in widely available, natural – not artificial – crystalline solids was not described so far. Their existence would complement their occurrence in quantum phase transitions. To this end, and in order to be concrete, we considered the transition from the face-centered-cubic (*fcc*) of cobalt (Co) to the hexagonal-close-packed (*hcp*) phase, and the transition from the body-centered cubic (*bcc*) of zirconium (Zr) and titanium (Ti) to the *hcp* phase. The transitions take place for Co when T is decreased below the critical temperature $T_c \approx 700\,\mathrm{K}$,[24,25] and for Zr and Ti when T is decreased respectively below $T_c \approx 1850\,\mathrm{K}$ and $T_c \approx 1155\,\mathrm{K}$.[26–31] The described structural transition involves a structural change of the primitive unit cell, both for artificial or natural crystals. The emerging of Goldstone and Higgs modes in natural crystals is not conceptually different from the same occurrence in artificial ones. Nevertheless, it is a further confirmation that the amplitude mode is a ubiquitous collective excitation in condensed-matter systems with broken continuous symmetry.[32]
In section 2 the theory is developed and this new perspective is presented and discussed. In the end, in section 3 the main ideas are summarized.

2 SSB and structural phase transitions

Very generally, the expansion of the total energy of crystal's atoms with mass μ_n around their equilibrium positions, displaced by $\vec{a}_n$ at temperature T, can be written as

$$\begin{aligned} E = \quad & \frac{1}{2}\sum_{n\hat{i}} \mu_n \left(\partial_t a_n^{\hat{i}}\right)^2 + \sum_{nm}\sum_{\hat{i}\hat{j}} Q_{nm;\hat{i}\hat{j}} a_n^{\hat{i}} a_m^{\hat{j}} \\ + \quad & \sum_{nmqr}\sum_{\hat{i}\hat{j}\hat{k}\hat{l}} R_{nmqr;\hat{i}\hat{j}\hat{k}\hat{l}} a_n^{\hat{i}} a_m^{\hat{j}} a_q^{\hat{k}} a_r^{\hat{l}} + ..., \end{aligned} \tag{3}$$

where the sum runs over the N atoms index $n \in \{1^{\hat{i}}, 1^{\hat{j}}, 1^{\hat{k}}, ...N^{\hat{i}}, N^{\hat{j}}, N^{\hat{k}}\}$, and $a_n^{\hat{i}}$ are the spatial components of $\vec{a}_n$. The first term is the kinetic energy of the atoms, the second term is the potential harmonic term, followed by the fourth order anharmonic term. The potential energy term, i.e. the second, and higher order terms, can be identified by the crystal free energy of the Ginzburg-Landau theory, and the $Q_{nm;\hat{i}\hat{j}}$ matrix describes the energy cost to shift the atoms away from their equilibrium position in the harmonic approximation. In a theoretical field approach, the displacements are defined by a complex vector field $\vec{\phi}$, and the free energy can be conveniently written in the spatial ϕ-components (with summation over repeated index, according to the Einstein's convention) as

$$F(\phi) = \frac{1}{2!}\mathcal{Q}_{\hat{i}\hat{j}}\phi^{\hat{i}}\phi^{\hat{j}} + \frac{1}{4!}\mathcal{R}_{\hat{i}\hat{j}\hat{k}\hat{l}}\phi^{\hat{i}}\phi^{\hat{j}}\phi^{\hat{k}}\phi^{\hat{l}} + O(|\phi|^6), \tag{4}$$

where

$$\mathcal{Q}_{\hat{i}\hat{j}} = \frac{\partial^2 F(\phi)}{\partial\phi^{\hat{i}}\partial\phi^{\hat{j}}}, \quad \mathcal{R}_{\hat{i}\hat{j}\hat{k}\hat{l}} = \frac{\partial^4 F(\phi)}{\partial\phi^{\hat{i}}\partial\phi^{\hat{j}}\partial\phi^{\hat{k}}\partial\phi^{\hat{l}}} \tag{5}$$

evaluated at equilibrium. Very generally and considering a three-dimensional crystal, we can rewrite the Equation (4) in a more compact way as

$$F(\hat{\phi}) = \frac{1}{2}\mathcal{A}\hat{\phi}^\dagger\hat{\phi} + \frac{1}{4}\mathcal{B}\left(\hat{\phi}^\dagger\hat{\phi}\right)^2 + O(|\hat{\phi}|^6), \tag{6}$$

where $\mathcal{A}$ and $\mathcal{B}$ are real coefficients, and ϕ is a field operator, the order parameter, which in coordinates is an atomic displacements matrix, whose rank and symmetry properties depends on the considered unitary cell.[33] It can be remarked that odd powers of $\hat{\phi}$ in the free energy expansion are customary excluded. This because, if ϕ is a complex wavefunction, the free energy cannot contain a phase in order to be an observable. This choice does not prevent important interactions to arise (like three-phonons coupling, phonons decay, etc.), and this important point will be clarified at the end of the present discussion: in particular, they are generated by nonlinear terms in Equation (13). For this reason, it is safe for the purpose of the present analysis to exclude those terms starting from Equation (3).
It is worth noticing that, within the frame of Ginzburg and Landau theory, Ref. [30] calculates from first principles the free energy difference $F(\phi)$ between the parent (*bcc*, symmetric) and the product phase (*hcp*, with broken symmetry) as

$$\tilde{F}(\phi) = \frac{A_0(T-T_0)}{2}\phi^2 + B\phi^4 + C\phi^6, \tag{7}$$

where ϕ is a scalar order parameter (of course, the same arguments would also apply to structural transition between *fcc* and the *hcp* phases). $\tilde{F}(\phi)$ was derived from a one-dimensional (or scalar) model, and it has the same functional form of the Equation (6), except for the fact that the expansion in powers of ϕ also retains the 6th order term. Here T_0 is a characteristic temperature, A_0 and C are real and positively defined parameters, whereas B is negative. In addition, it can be noticed that for $T < T_0$, also the coefficient of ϕ^2 is negative.
The Ginzburg and Landau theory, and even the Higgs mechanism, have no intrinsic limitations on the number of expansion terms of $F(\phi)$ in powers of ϕ, since both theories are phenomenological, and they offer a way to describe global symmetry breaking, therefore a second order transition, at least in their original formulations. Nevertheless, the same theory can be also applied to structural phase, first order transitions,[34] for which an expansion to the 6th order is customary, when an accurate fitting of the free energy and a description of the behavior around T_0 are required. However, this is not the focus of the present discussion: the main requirement for the present, phenomenological approach is to have the SSB correctly described, i.e. the properties of the structural phase for $T \ll T_0$ and for $T \gg T_0$. Nevertheless, it is important to consider and compare the two alternative forms,

$$F_1(\phi) = \quad \alpha_1(T-T_0)\phi^2 + \beta_1\phi^4 + \gamma_1\phi^6 \tag{8}$$
$$F_2(\phi) = \quad \alpha_2(T-T_0)\phi^2 + \beta_2\phi^4. \tag{9}$$

Regarding $F_1(\phi)$, in the broken phase *hcp* it must be $\alpha_1(T-T_0) < 0$, $\beta_1 < 0$, and $\gamma_1 > 0$. Conversely, $F_2(\phi)$ may describe the same broken phase only if $\alpha_2(T-T_0) < 0$ and $\beta_2 > 0$.
As a test, we can consider the 6th order expression $F_1(\phi)$ with parameters as in Ref. [30] for Ti, setting $T = 300\,\mathrm{K}$ (according to Ref. [30] it is $T_0 = 484.4\,\mathrm{K}$). The plot of $F_1(\phi)$ is reported in Figure 1(a), together with the plot of $F_2(\phi)$ with the coefficients α_2 and β_2 obtained from $F_1(\phi)$ with a nonlinear fitting algorithm. The purpose is to understand the differences between the behaviors of F_1 and F_2, far above and far below T_0. As expected according to the Ginzburg-Landau model (of the Higgs mechanism), for the quartic $F_2(\phi)$ we obtained $\alpha_2(T-T_0) < 0$, and $\beta_2 > 0$, and at least for a SSB description, the free energy described by $F_2(\phi)$ in the broken phase can be considered representative of the $F_1(\phi)$ expression: they both describe a system for which $\phi = 0$ is not a stable state. In this perspective, a $F(\phi)$ formulation as given by the Equation (1) correctly describes the situation according to the F_2 functional form,

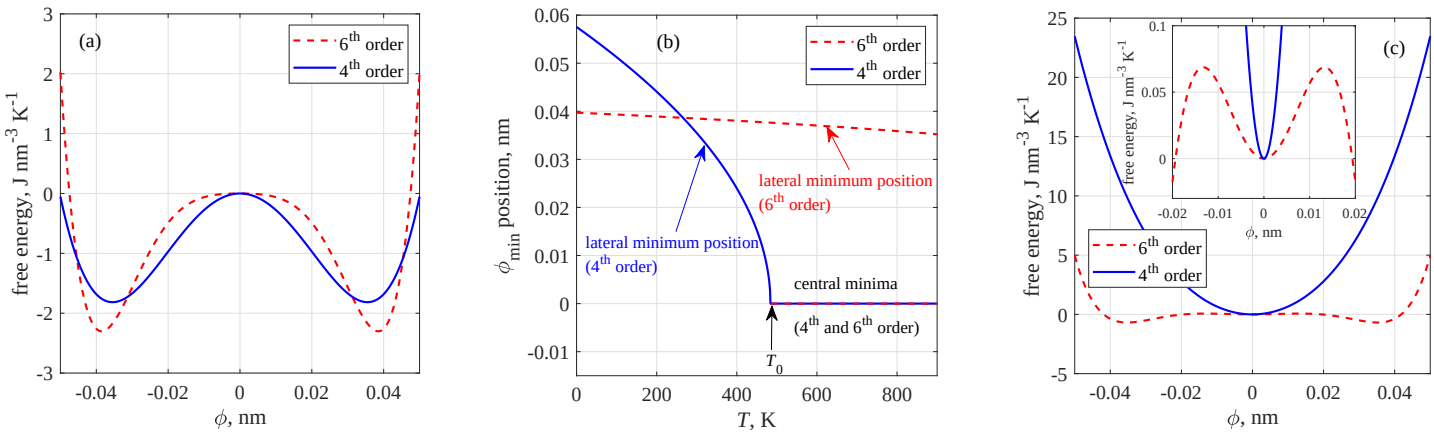

Figure 1: (a) Plots of the free energy according to $F_1(\phi)$ (for parameters as in Ref. [30] for Ti) and $F_2(\phi)$ (with parameters evaluated from $F_1(\phi)$ with a nonlinear fitting algorithm) for $T = 300\,\mathrm{K}$. (b) The position $\phi_{\min}$ of the positive minimum of the free energy (the negative minimum is symmetric) as function of T. When it exists, i.e. for $T > T_0$, the minimum in $\phi = 0$ is also reported, for clarity, for foth F_1 and F_2. In the panel (c), the plots of $F_1(\phi)$ and $F_2(\phi)$ is shown for $T = 900\,\mathrm{K}$, i.e. well above T_0, where in the inset the detail of the minimum in $\phi = 0$ (which has become a stable minimum) is better visible.

provided we identify the coefficients according to

$$-\mu_0^2 = \alpha_2(T - T_0)\,, \quad \frac{\lambda}{4} = \beta_2, \tag{10}$$

with $T < T_0$, $\alpha_2 > 0$, $\beta_2 > 0$, hence $\lambda > 0$.
A more substantial difference appears around the transition: for $T > T_0$, the order parameter disappears only for the quartic $F_2(\phi)$ (see Figure 1(b)), and this is a distinctive feature of second order phase transitions. Since we are considering instead a first order transition, for $T \approx T_0$ the *hcp* and *bcc* (or *fcc*) may coexist,[30] since for $T > T_0$ a stable minimum in $\phi = 0$ arises (for $T > T_0$, the second derivatives of both $F_1(\phi)$ and $F_2(\phi)$ are positive in $\phi = 0$).
However, regarding the present work, it is particularly important to examine what happens far from T_0. For $T < T_0$, both $F_1(\phi)$ and $F_2(\phi)$ allow for a stable stationary state only for $\phi \neq 0$: the system is in the *hcp* phase, and the state with $\phi = 0$ is unstable. In other terms, if we employ F_1 or F_2 as a potential in a quantum field theory of atomic vibrations, $\phi = 0$ is a false, unstable vacuum state, since an infinitesimal perturbation would bring the system to oscillate around one of the lateral minima $\phi \neq 0$, the only true and stable vacuum states. Conversely, for $T \gg T_0$, the quartic $F_2(\phi)$ has a unique minimum in $\phi = 0$, which corresponds to a stable vacuum. Regarding $F_1(\phi)$, although it still has three minima, $\phi = 0$ has become a stable minimum, i.e. the expectation value of ϕ in the true vacuum quantum state is zero. In summary, excluding the transition region $T \approx T_0$, when $T \gg T_0$ the true quantum vacuum state is in $\phi = 0$, whereas the relative minima in $\phi \neq 0$ (see Figure 1(c)) do not correspond to any true vacuum state.
It must be remarked that the description of the lattice structure around the transition is a complex problem, and its exhaustive treatment goes beyond the purpose of the present study, which deals with the investigation of the order parameter oscillations, well below and well above T_0. The purpose of the Ginzburg and Landau theory is just to provide a functional form suitable to describe phase transitions, distinguishing between a status in which the free energy has a *stable* minimum in $\phi = 0$ (symmetric phase), and a status in which the *stable* minimum lies in $\phi \neq 0$.
Following Ref. [21] and exploiting the similarities between the sonic (or acoustic) metric and the Lorentzian metric of the ordinary space-time,[35–40] the dynamics of $\hat{\phi}$ can be described by the Lagrangian density

$$\mathcal{L}_\phi = \frac{1}{2}\partial_\mu\phi^*\,\partial^\mu\phi - V(\phi) \tag{11}$$

$$V(\phi) = -\frac{\mu_0^2}{2}\phi^*\phi + \frac{\lambda}{4}\left(\phi^*\phi\right)^2 + V_c(\phi), \tag{12}$$

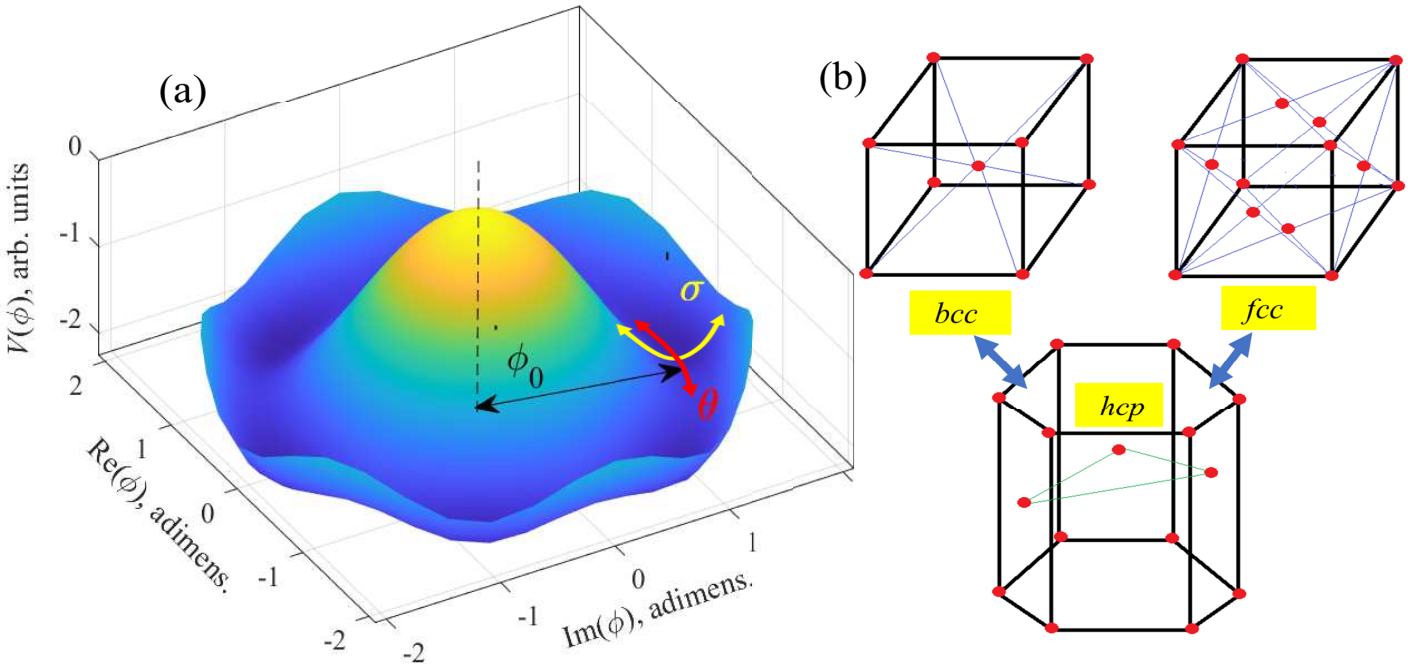

Figure 2: (a) The Higgs potential $V(\phi)$, leading to the excitation of the amplitude (or Higgs) and phase (or Goldstone) modes, σ and θ, for the *hcp* phase. (b) Illustrative scheme of *bcc*, *fcc*, and *hcp* crystal structures (the red dots represents the ions).

where the complex field ϕ in coordinates corresponds to the field operator $\hat{\phi}$. Moreover, we have identified the potential energy $V(\phi)$ with the crystal free energy in the *hcp* given by the simpler F_2 functional form, although nothing substantial would change if we adoped F_1, as discussed above, when commenting Figure 1). We included in the potential an additional term $V_c(\phi)$, which depends on the particular crystal we are considering. For example, in cubic crystal it is[41] $V_c(\phi) = \lambda_1 \left[\mathrm{Re}(\phi)\mathrm{Im}(\phi)\right]^2 = \lambda_1/4\,(\phi^*\phi)^2 \sin^2(n \arctan(\phi))$, where $n = 2$ and λ_1 is a constant. The effect of $V_c(\phi)$ consists in providing four couples of minima and maxima in the brim of the potential, in correspondence of ion positions. In hexagonal crystals it is $n = 3$, and there are six couples of local minima and maxima, but this is just a detail. What is important to consider is the effect that these minima may have on the final result. $V(\phi)$ has the "Mexican hat" shape (Figure 2(a)) typical of the Higgs SSB theory, a little modified by the $V_c(\phi)$ term. The Lagrangian $\mathcal{L}_\phi$ is still $U(1)$ invariant in a neighborhood of $\phi = 0$, but its symmetric vacuum state $\phi = 0$ is unstable. In case $\lambda_1 = 0$, all the values of ϕ in the circle of radius $\phi_0 = \sqrt{\mu_0^2/\lambda}$ are minima of $V(\phi)$ and the brim is flat. Here, the order parameter takes nonzero values, and the states $\phi = \phi_0 e^{i\theta}$ are the only stable vacuum states, all with the same energy. Among them, the system chooses the *ordered state* with a particular phase θ_0. For arbitrary value of λ_1, it corresponds to a local minimum of $V(\phi)$, which becomes the true vacuum state of the system. What is important to note, is that the vacuum state (ϕ_0, θ_0) is not $U(1)$ invariant, having broken the rotational symmetry described by the Lie group $U(1)$.

The Higgs SSB formalism described above, and the identification of $U(1)$ as the symmetry group for the Lagrangian, show that there is also a more fundamental reason for the choice of the quartic expression $F_2(\phi)$ as an appropriate potential. It is possible to demonstrate a theorem,[42,43] according to which, if G is a compact Lie group (in the present case, $U(1)$) which acts smoothly on the real manifold M with $\phi \in M$, the *orbit* $G(\phi)$ is critical, that is, every smooth real $\mathcal{G}$-invariant function on M is stationary on $\mathcal{G}(\phi)$ if and only if $\mathcal{G}(\phi)$ is isolated in its *stratum* (a *stratum* consists of all points of the same symmetry class). Very shortly and informally, we remind that an *orbit* $\mathcal{G}(\phi)$ is the ensemble of all points of M which can be reached from ϕ by a (eventually broken) symmetry transformation, that is, $\mathcal{G}(\phi) = \{g\phi | g \in G\}$. Two points on the same orbit have isotropy groups H_ϕ that are isomorphic (the isotropy group H_ϕ

is formed by the set of all group elements that leave ϕ invariant, that is, $H_\phi = \{g\phi = \phi | g \in G\}$: it is formed by those transformations which are left unbroken when the order parameter takes the value ϕ). Consequently, any potential V on the manifold M which is invariant under the group action, i.e. $V(\phi) = V(g\phi)$ for all $\phi \in M$ and $g \in G$, may be thought of as a function on the orbits: in this way, the minimization of a given potential $V(\phi)$ is reformulated as a minimization of a function on the space of orbits, and a transformation $\phi \to g\phi$ along one of the orbits does not cost energy: anticipating something, this will originate the Goldstone boson. Changing orbit, an energy cost must be paid, and this will give rise to the Higgs boson, for which a mass term is expected. An interesting fact for our discussion is that "the theorem makes no particular assumption about the form of the invariant function, so it may be a Higgs-type quartic potential as well as the full quantum effective potential whose power expansion may contain terms of arbitrarily high orders in ϕ".[43]
With reference to Figure 2(a), we can expand $\mathcal{L}_\phi$ around the vacuum (ϕ_0, θ_0) in terms of small oscillations σ and θ (here $\arctan(\phi)$ can be expanded around the minimum as $\theta/\sqrt{\phi^*\phi}$), obtaining the Lagrangian density

$$\begin{aligned} \mathcal{L}_{\sigma\theta} = & \quad \frac{1}{2}\left(\partial_\mu\theta\,\partial^\mu\theta - \frac{\lambda\theta^4}{2}\right) \\ + & \quad \frac{1}{2}\left(\partial_\mu\sigma\,\partial^\mu\sigma - 2\mu_0^2\sigma^2 - 2\mu_0\sqrt{\lambda}\sigma^3 - \frac{\lambda\sigma^4}{2}\right) \\ - & \quad \mu_0\sqrt{\lambda}\sigma\theta^2 - \frac{\lambda}{2}\theta^2\sigma^2 + \frac{\lambda_1}{4}\left(\sigma^2+\theta^2\right)\theta^2\,, \end{aligned} \tag{13}$$

that can be simplified neglecting nonlinear terms higher than second order:

$$\mathcal{L}_{\sigma\theta} = \frac{1}{2}\partial_\mu\theta\,\partial^\mu\theta + \frac{1}{2}\partial_\mu\sigma\,\partial^\mu\sigma - \mu_0^2\sigma^2. \tag{14}$$

When plugged into the Euler-Lagrange equations, Equation (14) provides two oscillatory solutions for the fields θ and σ. The solution of θ is a phase oscillation mode along the Mexican hat brim, with frequency dispersion relation $\omega^2 = c_s^2k^2$, and it is a Nambu-Goldstone mode (c_s is the sound velocity in the crystal). There is no mass term, hence the dispersion relation is gapless. The solution for σ describes amplitude oscillations, and it is a Higgs mode, whose frequency dispersion relation is $\omega^2 = 2\mu_0^2 + c_s^2k^2$. It is gapped, since in the Lagrangian there is a mass term, $\mu_0\sqrt{2}$.
The field θ is a pure gauge field, and we identify it with the *acoustic* phonon, arising as the Goldstone mode associated to the breaking of the continuous translational invariance due to the lattice itself.[44,45] It is a massless gauge mode, because it is possible to change the ground state of θ without spending energy, just operating a gauge transformation along the valley of the Mexican hat. A different scenario may take place when terms proportional to λ_1 cannot be neglected. In this case, nonlinearities brought by λ_1 have two effects: firstly, the additional term proportional to $\lambda_1\theta^4$ in the Equation (13) makes the frequency dispersion of the Goldstone mode θ to become gapped, $\omega^2 = \rho^2\sqrt{\lambda_1 c_s^2/2} + c_s^2k^2$, where ρ is an integration constant which depends on the cell details.[21] Secondly, the other additional term proportional to $\lambda_1\sigma^2\theta^2$ in the same equation describes the coupling between Goldstone and Higgs modes, as described in Ref. [21] for general nonlinearities, and the effects can be important in systems where phonons couple heavily to strain field. Instead, regarding the Higgs mode, we propose to identify it with the *optical* phonon, whose frequency in the long-wavelength limit is given by the "mass" term, $\omega_0 = \mu_0\sqrt{2}$. The experimental phonon dispersion of Co, shown at room temperature in Ref. [24] and at 833 K in Ref. [25] confirm that the optical phonon branches exist only at the lowest temperature. Unlike for the high energy physics, the hidden symmetry can be restored very simply: it is enough to increase the temperature above the value of T_0 characteristic of the considered crystal (in our examples, Zr, Ti, Co): a *hcp* $\to$ (*bcc, fcc*) structural phase transition takes place, and in the (*bcc, fcc*) symmetric phase the coefficient of the quadratic term in $F_2(\phi)$ becomes positive. In this case, the expectation value of ϕ in the physical vacuum state is $< \phi_0 >= 0$, and the system has recovered the $U(1)$ invariance, that in the *hcp* phase was broken. The only relevant broken continuous symmetry is the translational symmetry, which still makes

a Nambu-Goldstone mode to emerge, the *acoustic* phonon, but no Higgs mode exists, as experimentally verified for Co at $T = 833\,\mathrm{K}$ in Ref. [25], where the structural phase becomes *bcc*, and only the acoustic phonon branches survives. Similar considerations and experimental results can be found in literature con Zr and Ti (*fcc* $\rightarrow$ *hcp*).[24–28,46] Despite its much simpler formulation, the hidden symmetry restoration represented by the *hcp* $\rightarrow$ (*bcc, fcc*) phase transition when temperature increases above T_0 is conceptually similar to what happens in the Standard Model for the electroweak interaction above the electroweak symmetry breaking energy ($\approx 159\,\mathrm{GeV}$[47]).
The number of oscillating modes for θ and σ depends on the crystal unitary cell, and on the dimension of the matrix associated with the operatorial form of the order parameter $\hat{\phi}$. In the considered examples, the crystal broken phase is *hcp*, and following Ref. [33] it is possible to write the displacement matrices Q's evaluated at symmetry points of the Brillouin zone. They can be employed to build the dynamical matrix as blocks of submatrices, substantially the Q's themselves. The dynamical matrix has six eigenvalues, and so it is for the matrix associated with $\hat{\phi}$ at the same symmetry points. In the ground state of the broken phase, there will be three eigenvalues belonging to θ and three belonging to σ. Hence, there will be three fields θ (acoustic branches) and three fields σ (optical branches). For each branch, two fields represents oscillations in the *hcp* basal plane (transversal modes), and one field represents an oscillation orthogonal to the plane (longitudinal mode).
An important point that can be recalled is the fact that the Equation (13) also describes three-phonons scattering terms (the terms proportional to θ^3 and to σ^3) and four-phonons scattering terms (the terms proportional to θ^4 and to σ^4), coming fron anharmonicities. They also describe the acoustic-optical phonon coupling and decay (the terms proportional to $\sigma\theta^2$ and to $\theta^2\sigma^4$), as described more extensively in Ref. [21].
As a side note, even having conceptually identified the free energy with the Higgs potential, in general it is not possible to associate a specific type of phonon with the Higgs and Goldstone modes.[23] In fact, since $Q_{n,m}$ is the force constant matrix, its value depends on the atomic masses in the unitary cell, and the phonons are eigenvectors of $Q_{n,m}/\sqrt{\mu_n\mu_m}$, that correspond to Goldstone and Higgs modes according to our description only in case the crystal contains atoms of only one mass μ_n, as in the examples considered in the present work (crystals of Co, Zr, Ti). In summary, the phase (or Goldstone) and amplitude (or Higgs) oscillations always originate from a SSB, but only in some special cases it is possible to associate them with a clear character of acoustic and optical phonon.[22,23] In the present work, we identified them in some example of natural crystals.

3 Conclusions

We described the occurrence of Goldstone and Higgs modes in clearly identifiable *structural* phase transitions occurring in widely available, natural – not artificial – crystalline solids.
Expanding the total energy of crystal's atoms around their equilibrium positions, we identified the potential energy term with the crystal free energy difference $F(\phi)$ between a parent, symmetric phase, and a product phase with broken symmetry, within the Ginzburg-Landau theory formalism.
When the initial system's symmetry is broken during the phase transition to the *hcp* phase, Goldstone (phase) and Higgs (amplitude) modes arise. In the special case of crystals made of one atomic species only, these modes can be identified with the acoustic and optical phonons.
This perspective offers an example of what in the Standard Model of particle physics is difficult to achieve, i.e. the symmetry restoration. In fact, a higher crystal symmetry, hidden in the *hcp* broken phase, can be easily restored by increasing the temperature above T_0: a phase transition to a more symmetric *bcc* or *fcc* phase makes again $U(1)$ invariant the Lagrangian density, beside making stable the symmetric vacuum state where the expectation value of ϕ is $< \phi_0 >= 0$.

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