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Condensed matter physics in the 21st century: The legacy of Jacques Friedel

Structure of covalently bonded materials: From the Peierls distortion to Phase-Change Materials

Structure des matériaux covalents : de la distorsion de Peierls aux matériaux à changement de phase

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ABSTRACT

The relation between electronic structure and cohesion of materials has been a permanent quest of Jacques Friedel and his school. He developed simple models that are of great value as guidelines in conjunction with *ab initio* calculations. His local approach of bonding has both the advantages of a large field of applications including non-crystalline materials and a common language with chemists. Along this line, we review some fascinating behaviors of covalent materials, most of them showing a Peierls (symmetry breaking) instability mechanism, even in liquid and amorphous materials. We analyze the effect of external parameters such as pressure and temperature. In some temperature ranges, the Peierls distortion disappears and a negative thermal expansion is observed. In addition, the Peierls distortion plays a central role in Phase-Change Materials, which are very promising non-volatile memories.

RÉSUMÉ

La relation entre structure électronique et cohésion des matériaux a été un sujet d'étude permanent de Jacques Friedel et de son école. Il a développé des modèles simples, intuitifs qui se sont révélés des guides d'une grande valeur et par la suite un complément utile aux calculs ab initio.

Son approche locale de la liaison chimique s'applique à un vaste champ de systèmes, incluant les matériaux non cristallins et permis un langage commun avec les chimistes. Dans cet axe nous passons en revue quelques comportements fascinants des matériaux covalents, la plupart d'entre eux présentant un mécanisme d'instabilité de Peierls (brisure de symétrie), même les liquides et les amorphes, étonnamment. Nous analysons aussi l'effet de parame'tres externes tels que la pression et la température. Dans un certain domaine de température, la distorsion de Peierls disparaît et une dilatation thermique négative est observée. Enfin, la distorsion de Peierls joue un rôle central dans les matériaux

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à changement de phase (PC materials), qui sont très prometteurs pour la réalisation de mémoires non volatiles.

1. Covalent materials: structure–cohesion–electronic properties

Covalent materials have shown a constantly renewed interest in the last seventy years, mainly because of their electronic properties. Jacques Friedel and his school studied extensively the relation between structure, electronic structure and cohesion of covalent materials using simple, elegant models of the cohesion. A semi-empirical quantum mechanical model (with a limited number of parameters) has the advantage of being applicable to a large series of structures, crystalline and non-crystalline, liquid, surfaces, clusters.... The tight-binding approximation of independent electrons has proven very successful and applicable to a large variety of situations. Following a very first application on the band structure of semiconductors [1], the model has been generalized to amorphous semiconductors [2,3]. Extensive applications have been made in the field of semiconductor surfaces and defects [4]. The octet rule $Z = 8 - N_{\rm sp}$, where Z is the coordination number and $N_{\rm sp}$ is the number of s and p electrons in the valence shell was demonstrated along these lines [5].

We shall mainly focus on elements of columns V, VI and VII of the periodic table. They are covalent materials, and their crystal structure may be viewed as a distorted, simple cubic one (Fig. 1). We will show that this originates from their electronic structure and the directionality of the p-orbitals. The distortion arises from a symmetry-breaking mechanism related to the Peierls distortion.

The Peierls distortion (PD) is an instability of one-dimensional metals. It is explained by J.-P. Pouget in the present issue [6,7] and in [8]. The mechanism is summarized in Fig. 2 below.

The periodicity of the Peierls distortion depends on the filling of the band or the number of electrons per atom e/a as illustrated in Fig. 1. The role of e/a on the crystallographic structure has been considered previously by Hume-Rothery as emphasized by Jacques Friedel. The Peierls distortion has been first described in his lectures notes (Les Houches, 1953, see inset in Fig. 2) and later in a textbook [9].[1] However, the idea of a symmetry breaking mechanism in group V elements (Bi) has been considered by H. Jones [10] as early as 1934 and discussed in the celebrated book of Mott and Jones [11].

In this paper, we extend the concept of Peierls distortion to three-dimensional systems, we derive its condition of occurrence and its importance when it is present or vanishes.

2. Minimal model of distortion

The two ingredients of the chemical bond or cohesion, namely electromagnetism and quantum mechanics, are well established, but due to the fact that many electrons and nuclei are interacting, the problem has no exact analytic solution. Consequently, there are different theories of cohesion and various levels of approximation. In a minimal model, the covalent bond can be simply described by a sum of two energies: an attractive part due to the resonance of the valence orbitals (s and p in covalent materials), described by a resonance integral $\beta(r)$ and a pairwise additive repulsive potential $V_{\rm rep}(r)$. Both are decreasing functions of the distance and are expressed by a power law [12] or an exponential function.[2]

$$\beta(r) = \frac{\beta_0}{r^q}$$
$$V_{\rm rep}(r) = \frac{V_0}{r^p} \tag{1}$$

with $p > q$. The attractive (electronic) part originates from the band broadening by resonance. Typical values of the q parameter are between 2 and 3 for covalent materials [12]. Let us stress the importance of the repulsive term in the structure of materials [13], especially when a distortion appears. The repulsive term is usually neglected in the chemical literature and the experimental equilibrium distance is taken [14]. It is difficult to model the repulsive energy as it originates not only from the electrostatic repulsion but also from Pauli's exclusion principle. The hardness of the repulsion is characterized by the exponent p.

Let us start with a very simple model that contains all the ingredients of the symmetry-breaking mechanism and that shows under which conditions the highest symmetry (or highest coordinated) structure is the most stable. In 1D, 2D or 3D in a system with Z neighbors, with isotropic interactions, the second moment (variance) of the electronic density of states $n(E)$ is $Z\beta^2$, hence the bandwidth is proportional to $\sqrt{Z}\beta$ (second moment approximation [15]). This is a consequence of the quantum mechanical character of the covalent bond. With a pairwise additive repulsive term the total energy writes, per atom:

[1] But he never published it in a research paper.

[2] The relevant parameter is the dimensionless logarithmic derivative of the function, β or V, at the equilibrium separation.