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On the formation of structure and electronic transport

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Abstract

By systematic studies of amorphous systems (and most of the results are transferable to liquid systems) we are able to show that structure formation at early stages is to a high degree the effect of self-organized and hence optimized resonances between macroscopic subsystems. There is, for example, a spherical-periodic resonance, based on momentum exchange between the valence electrons in total as one subsystem, and the forming static structure as the other one. It causes spherical structural periodicity of nearest-neighbour shells at medium distances and is a global effect, giving rise to similar effects as described by Bloch's theorem in crystals. Resonances based on an exchange of angular momentum became apparent too. Accordingly, together with the local quantum chemical effects, global resonances are important as well and both will cooperate to get the most optimal energetic situation for the total system. Occasionally, the global effects even dominate structure formation. We report on different scenarios where the total system is able to optimize the resonances. The resonance model explains major structural features of many liquid and amorphous systems of different types as there are pure elements, binary as well as ternary alloys, metallic glasses, glassy semiconductors, glassy Zintl systems, and light-weight Al–TM alloys (TM: from Ti to Cu). Spherical-periodic order causes pseudogaps or even gaps at the Fermi energy and hence has dramatic influences on any electronic transport. Accordingly, understanding structure formation on the basis of resonances also triggers a deeper understanding of electronic transport properties.

Keywords: A. Alloys; A. Amorphous materials; C. Electron diffraction; D. Electronic structure

1. Introduction

Very commonly one assumes that during structure formation at early stages the individual atoms and their interaction play a major role. Quantum chemistry, describing these local chemical effects, is extremely powerful. Indeed, whenever we deal with a small number of atoms ($n<50$) the formation of larger, still tiny entities is well understood by solving Schrödinger's equation. Solving this equation, on the other hand, is nothing else but finding a local resonance between the location of the atoms (their static structure) and the distribution of the electrons (the electronic structure). The energetic states of the total system get split into bonding states and anti-bonding states, where the former gets occupied. But, whenever a huge number of atoms ($n \gg 50$), with unknown starting positions, necessary for an adequate description of condensed matter at its path to a crystal, may agglomerate, solving Schrödinger's equation becomes impossible. Hence, unfortunately, local quantum chemistry is left as the only tool. Global effects, if they exist, cannot be treated properly. For sure, as more experimental information as e.g. the density, or cleverly chosen local structural entities were introduced, the larger can n be chosen. Consequently, fundamental processes at early stages as well as the evolution of disordered systems to the crystalline state are not well understood. The same holds true for the related formation and evolution of electronic transport and many other properties.

When a crystal finally has been formed and shows planar periodicities, again we can well describe its stability by solving Schrödinger's equation, but now for a few particles within the unit cell, after we have additionally applied

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Bloch's theorem. Unfortunately, the unit cell itself has in advance been determined experimentally and the process of its formation, the reasons for its stability, hence, has not really been understood. Indeed, what is often forgotten is that periodicity itself introduces a new stabilizing effect, not described by local quantum chemistry, namely global resonances between macroscopic subsystems, as there are the forming static structure as the one and the valence electrons in total as the other one [1]. The former gets described by the spacing d between the atomic planes, the latter by the Fermi wavelength λ_F. Both are global properties. The resonance is based on momentum exchange between the subsystems and forms gaps in the electronic dispersion at the Brillouin-zone boundary [2]. Solving Schrödinger's equation under the help of Bloch's theorem is nothing else than finding those global resonances which are cooperating with the local ones. Accordingly, applying Bloch's theorem expresses the dealing with a system affected energetically also by global resonances.

The question now arises, how do we have to describe disordered systems? The most effective procedure namely the reduction of the huge number of parameters by Bloch's theorem will, at a first glance, not work since planar periodicities do not yet exist. Is there something similar or can the formation of structure at this stage only be described by local effects?

Since disordered systems are the precursors of any crystal, understanding processes of their structure formation is of particular importance. Accordingly, the study of fundamental structure-forming processes at the very early stages [3], the evolution of structure to the crystalline state [4], the correlated formation and evolution of electronic transport properties [5], including many of their anomalies, are of high importance. Disordered systems are model systems, quite flexible to adjust mutually their subsystems to the optimal energy gain, to the strongest resonance splitting (under the given constraints).

We report on an effect among the global subsystems mentioned above, very similar to the planar resonances, namely a *spherical–periodic resonance*, causing spacially limited *spherical–periodic order* (SPO) in the mean around any atom. In r-space the SPO can best be seen by a sequence of nearest neigbour shell positions at $r_n = (5/4 + n) \cdot \lambda_{Fr}$, with $n = 0, 1, 2, \ldots$ [6]. The Friedel wavelength $\lambda_{Fr} = 2\pi/2k_F$, half of λ_F, describes the distances between the corresponding minima in the pair potential. $2k_F$ itself is related to the electron density $n_e = n_o\bar{Z}$ by $2k_F = 2\sqrt[3]{3\pi^2 \cdot n_e}$, with n_o the particle density and $\bar{Z}$ the mean valency of the atoms.

We are able to describe and even predict major aspects of the static structure of the disordered state of metals (e.g. a-SnAu) and semiconductors (e.g. a-GeSb), of ionic systems (e.g. a-SnNa), as well as light-weight Al–TM alloys (e.g a-AlFe), all of them on the same roots. Amorphous quasicrystals (e.g. a-AlCuFe) are reported elsewhere [7], amorphous Heusler/Half-Heusler alloys (e.g. a-AlNiTi) are under preparation to get published.

2. Experimental details

Thin films were prepared by sequential flash-evaporation onto substrates held at the temperature of l-He or l-N_2. Structure (measured by electron diffraction) and electronic transport were mostly measured in situ of the preparation chambers. Stable samples have been measured ex situ in a Philips CM20FEG. Details are described elsewhere [8].

3. Results and discussions

In Fig. 1 we show structural data for four completely different alloys, each representing its own class of disordered systems: those with s,p-electrons at E_F, but a minor contribution of d-states (a-SnAu) or no d-states at all (a-SbGe), those with charge transfer and ionic bonding features (a-SnNa), and those where one of the constituents starts structure formation with empty d-states at E_F (a-AlFe). In the third row n_o as well as $\bar{Z}$ is shown, both are input data for calculating the internal scales.

For SnAu (Fig. 1a) it is obvious that in the amorphous range there is a resonance-induced structural peak at K_{pe} (upper full line with dots), seen by its shift parallel to the varying $2k_F$. The $2k_F$ has either been estimated by the mean particle density n_o^{th}, taken from the individual atomic volumes of the constituents (dotted line) or by the experimental density (Fig. 1a(3)) (full line in Fig. 1a(1) without dots). For a-SnAu both differ although quite general density anomalies in this class of glassy metals are small or do not exist at all. The valencies can be taken from the position of the elements in the periodic table ($Z_{Sn} = 4e/a$, $Z_{Au} = 1e/a$) and are taken as unchanged by the presence of the other element (Fig. 1a(3)). Accordingly, for this type of metallic glasses the electronic system is quite inflexible and shows no or minor adjustments to the static structure.

In r-space, within experimental resolution, all the nearest-neighbour shells are closely related to the Friedel minima, calculated by n_o^{th} (dotted lines) or by n_o^{exp} (solid thick lines). The electronic system obviously triggers the equidistant position of the shells causing SPO. The periodicity at medium distances is responsible for the structural peak in k-space at $2k_F$. At 73.5 at% Au ($\bar{Z} = 1.8e/a$) the system is completely dominated by the global resonance. Now all the peak positions (in k-space, as well as in r-space) are in best agreement with the electronic constraints, even the first one. But, the first nearest-neighbour distance itself is by 25% larger than all the following shell distances, characteristic for SPO. This overall agreement clearly indicates SPO as a global collective effect. Altogether there are more than 50 different liquid and amorphous alloys known of this type and there is no one that does not behave similarly [13].

In the case of a-SnNa (Fig. 1b), additional to the adjustment of the static structure to the electronic constraints, the electronic subsystem is adjusting to the