Electron Localization in Solid-State Structures of the Elements: the Diamond Structure

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easily verify this result half quantitatively using a model kit as analog computer. The different sizes of C and Si are simulated with tetrahedral joints whose arm lengths differ[8] and the atoms are joined by flexible bonds (bent bonds).

In disilabicyclo[1.1.0]butane $C_2Si_2H_6$ (2) the region between the two C atoms does have a high ELF value (Fig. 1c and 1d). This confirms the previously described bond.[2] The relatively small region of high ELF values implies a weak bond, in agreement with the long bond length. The white ELF maximum is also clearly off the straight topological C–C connecting line. Its position is remarkably close to that of the bent bond derived from the simple structural model.[2] As expected, there is no bond between the Si atoms (Fig. 1d).

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Electron Localization in Solid-State Structures of the Elements: the Diamond Structure**

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The methods for obtaining localized orbitals—often used in the chemistry of molecules to describe bonding—can be

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used in principle for solids as well (in methane and in diamond, for example). They can lead, however, to several equivalent sets of orbitals for a given structure and are non-unique in this case. This ambiguity occurs, for example, in monomeric monocycles such as benzene, or in an infinite polyene chain.[11] In solids ambiguity often arises on account of the higher coordination, and localized orbitals are therefore used only rarely. An analysis in positional space can nevertheless be performed when instead of the equivocal localized orbitals, the electron localization function (ELF) is used. In this work we have calculated ELF for crystalline solids for the first time.

The electron localization function was introduced by Becke and Edgecombe as a measure of the probability of finding an electron in the neighborhood of another electron with the same spin.[2] ELF is thus a measure of the Pauli repulsion. The explicit formulation is given in Equation (a)

$$ELF = [1 + [K(r)/K_h(\varrho(r))]^2]^{-1} \qquad (a)$$

The parameter K is the curvature of the electron pair density for electrons of identical spin, $\varrho(r)$ the density at (r), and K_h the value of K in a homogeneous electron gas with density ϱ. The ELF values lie by definition between zero and one. Values are close to 1 when in the vicinity of one electron, no other with the same spin may be found, for instance as occurs in bonding pairs or lone pairs. Small values are typical for the region between two electron shells (Pauli principle). In a homogeneous electron gas, ELF = 0.5.

The method of local density functionals (LDF)[3,4] has proved exceptionally reliable for studies on solids. But in LDF the pair density and its curvature K are not explicitly defined. ELF may, however, be interpreted differently from (a), in order that the determination of its value is compatible with the LDF method. In this method (Kohn and Sham[6]) the single particle density matrix γ [Eq. (b)] is determined by energy minimization for a given electron density $\varrho(r)$ [φ are

$$\gamma(r,r') = \sum_i^N \varphi_i(r) \; \varphi_i(r') \qquad (b)$$

orbitals, N is the number of electrons; $\gamma(r,r') = \varrho(r)$]. Because $\gamma(r,r')$ occurs only in the expression for the kinetic energy T [Eq. (c), ∇ is the Nabla operator], the pertinent information

$$T = \tfrac{1}{2} \int \nabla_r \; \nabla_{r'}\gamma(r,r')|_{r=r'} d^3r \qquad (c)$$

is contained in the three-dimensional kinetic energy density $t(r,r')$ [Eq. (d)] and the six-dimensional function $\gamma(r,r')$ is not required.

$$t(r) = \tfrac{1}{2}\nabla_r \; \nabla_{r'}\gamma(r,r')|_{r=r'} \qquad (d)$$

The function $t(r)$ cannot exceed a certain threshhold,[7] which is defined by Equation (e). This minimum value occurs

$$t(r) \geq \frac{1}{8}\frac{|\nabla\varrho|^2}{\varrho} \qquad (e)$$

when the orbitals are proportional to $\sqrt{\varrho}$. According to the Pauli principle this is possible for at most two orbitals, one

with α and one with β spin. Thus in general the deviation is positive [Eq. (f)]. We shall call it the Pauli kinetic energy

$$t_P(r) = t(r) - \frac{1}{8}\frac{|\nabla \varrho|^2}{\varrho} \qquad (f)$$

density.[8] In some regions of space t_P tends toward zero, and we say that here the electron pairs are localized. Using t_P we can find a well-defined measure which corresponds to the ELF calculated from the Hartree–Fock approximation [Eq. (g)]. The parameter $t_{P,h}$ represents the value of t_P for a homogeneous electron gas with density $\varrho(r)$.

$$\text{ELF} = [1 + [t_P(r)/t_{P,h}(\varrho(r))]^2]^{-1} \qquad (g)$$

For the graphical representation we used, as we did previously for molecules, a program[10] that depicts the electron density and ELF values by the density of the points and their color, respectively. As in a map the colors range from blue (small ELF values) through green, yellow, and brown, to white (high ELF peaks). The background is black. Of the calculated electron density, only the valence electron density is illustrated. For this reason the (white) regions arising from

the inner shells around the nuclei are missing in Figure 1. Instead each nucleus is surrounded by a blue-violet bubble.

In this first report on ELF for solids, the diamond structure is investigated. Figure 1 shows the electron density and the ELF in the (110) plane. This plane contains the zig-zag chains of directly connected atoms and the essential details of the three-dimensional structure. In Figure 1a (diamond) regions of high localization (white) are seen on the lines joining the C atoms—the electron pair of the C–C bond. The framed exerpt serves to illustrate the differences when the atoms are Si, Ge, and α-Sn (Figs. 1b–d). Along this series the white regions of the covalent bonds become smaller, and the green waist (Si, Fig. 1b) gives way to a brown area. The effect is to create channels of evenly distributed localization analogous to an electron gas. Here we should point out that the topology of the wavy, three-dimensional, blue-green region corresponds completely to that of the space-dividing periodic nodal surface D*, which in turn is determined by the three-dimensional symmetry alone.[11] Thus there exists a three-dimensional periodic surface of the same electron density[11] as well as a corresponding surface of identical ELF values that has nothing to do with the contours of the atoms, but is defined only by the symmetry of the translational group.

The tetragonal structure of metallic tin (β-Sn) is related to the diamond structure. Also present are the essential details of the (110) plane. The zig-zag chains of the diamond structure meet in this plane. Figure 1e shows that in metallic β-Sn, the (white) regions of high localization have disappeared, and joining the chains are found (yellow) regions of localization similar to an electron gas. The change in the electron localization function along the series from carbon to tin thus shows spatially the characteristic transition from covalent to metallic bonding.
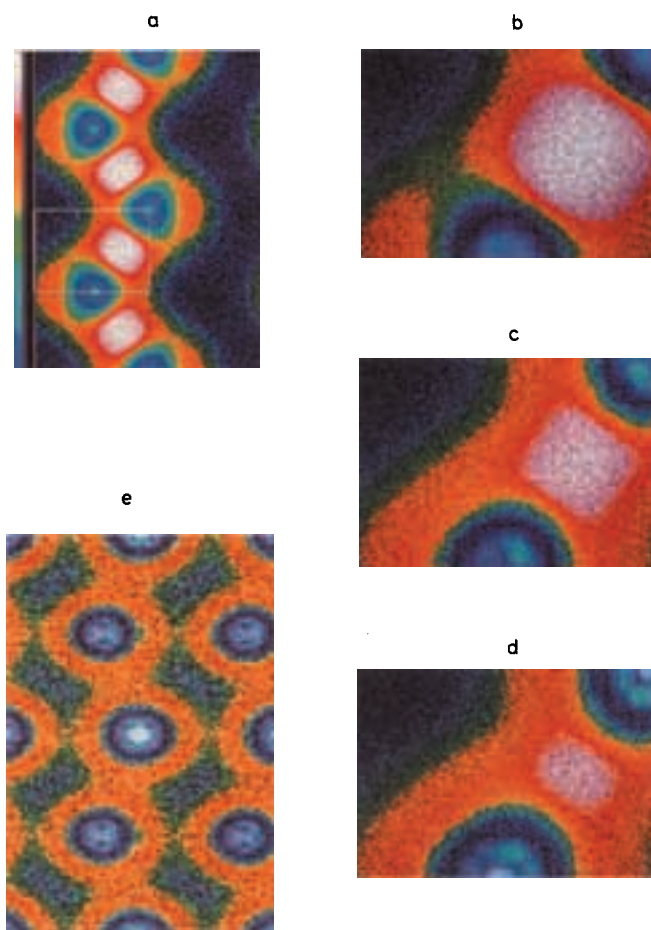
Fig. 1. Valence electron density ϱ (as "cloud") and ELF (depicted by color) for elements with diamond-type structures and for β-Sn. (Increasing ELF scale: blue, green, yellow, brown, white; background black; the blue regions around the nuclei arise from the missing inner shells) a) Diamond: the white regions represent C–C bonds; the small framed exerpt shows the section for the frames b) to d). b) Silicon. c) Germanium. d) α-Sn. e) β-tin; the white regions are no longer visible, and the chains show only a moderately high localization (orange-yellow). Interactions exist between the chains.

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