Laplacian and bond critical point properties of the electron density distributions of sulfide bonds: A comparison with oxide bonds*

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ABSTRACT

Topological and bond critical point properties of electron density distributions, \( \rho(r) \), were calculated for a series of sulfide molecules, containing first- and second-row main group M-cations. Laplacian maps of the distributions, \( \nabla^2 \rho(r) \), show that the valence shell charge concentration (VSCC) of the sulfide anion is highly polarized and extended into the inter-nuclear region of the M-S bonds, coalescing with the VSCCs of the more electronegative first-row cations. On the other hand, maps for a corresponding set of oxide molecules show that the oxide anion tends to be less polarized and more locally concentrated in the vicinity of its valence shell, particularly when bonded to second-row M-cations. A search for extrema in the \( \nabla^2 \rho(r) \) distributions reveals maxima in the VSCCs that can be ascribed to bonded and nonbonded electron pairs. The different and distinctive properties of sulfides and oxides are examined in terms of the number and the positions of the electron pairs and the topographic features of the Laplacian maps. The evidence provided by the electron density distributions and its topological properties indicates that the bonded interactions in sulfides are more directional, for a given M-cation, than in oxides. The value of the electron density distribution at the bond critical point and the length of a given M-S bond are reliable measures of a bonded interaction, the greater the accumulation of the electron density and the shorter the bond, the greater its shared (covalent) interaction.

INTRODUCTION

The sulfide anion differs from its congener oxide anion in several distinctive ways: (1) the radial probability density distribution of its valence orbitals is relatively diffuse and extended in space whereas that of the oxide anion is more localized in a region closer to the anion; (2) its dipole polarizability is roughly four times larger than that of the oxide anion; (3) its radius is larger; and (4) its electronegativity is smaller (Kutzelnigg 1984). Given these differences, it is not surprising that the crystal chemistry of the sulfides is different and distinct from that of the oxides (Wuench 1974). As one example, silicates and thiosilicates differ in several important ways: (1) silicates are common and widespread in nature whereas thiosilicates have yet, to our knowledge, to be reported as naturally occurring minerals, (2) silicates crystallize with a wide variety of structure types whereas thiosilicates adopt a much more limited variety of structures, (3) silicates with condensed tetrahedra exhibit a relatively wide range of bridging Si-O-Si angles (120°–180°) whereas thiosilicates exhibit a much more restricted range (105°–115°), and (4) SiO2 is a good glass-forming material whereas the glass forming tendencies of SiS2 are not as good (cf. Geisinger and Gibbs 1981; Kaftory et al. 1998 and references therein). On the other hand, despite the observation that the quadratic force constant of the longer Si-S bond (~300 N/m) is smaller than that of a comparable Si-O bond (~600 N/m), the range of Si-S bond lengths (2.02 to 2.21 Å) recorded for the thiosilicates is similar to that recorded for the silicates (1.57 to 1.72 Å; Liebau 1985; Gibbs et al. 1987a; Hill et al. 1994; Kaftory et al. 1998). In addition, the bond lengths calculated for oxide and sulfide molecules containing main group M-cations match those observed for crystals fairly well (Gibbs et al. 1987b; Bartelmehs et al. 1989). These bond lengths, \( R \), also correlate with the strength of the bonds, \( p \), \( \rho = s/r \) where \( s \) is the Pauling (1929) bond strength and \( r \) is the row number of the M-cation] according to the power law expression \( R = a \rho^{\beta} \) where \( \beta \approx 0.22 \) and \( \alpha = 1.39 \) and 1.84, respectively, for M-O and M-S bonds (Gibbs et al. 1987b; Bartelmehs et al. 1989). In a study of the power law relationship between \( p \) and the accumulation of electron density along the bonds in oxide molecules and crystals, Gibbs et al. (1998b) found that \( p \) correlates with the average value of the electron density, \( \rho(r_c) \), at the bond critical points, \( r_c \), of the M-O bonds forming the coordinated polyhedra in these materials, the larger the value of \( p \), the greater the average value of

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