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Electronic structure of thiospinel minerals: results from MO calculations

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Abstract

Molecular orbital calculations employing the SCF-X_α scattered-wave cluster method have been used to model the electronic structures of the thiospinel minerals linnaeite (Co_3S_4), carrollite ($CuCo_2S_4$) and greigite (Fe_3S_4). The results, which are in agreement with previously postulated qualitative models, support mixing of highest energy occupied orbitals (octahedral site e_g and tetrahedral site e orbitals) in Co_3S_4 and $CuCo_2S_4$ with consequent metallic conductivity and temperature independent (Pauli) paramagnetism. This contrasts with Fe_3S_4 in which spin-splitting of the orbitals in the valence region results in localized outermost electrons and ordered magnetism. The physical properties of thiospinels can be understood in terms of these molecular orbital models.

Introduction

Sulfides with the spinel crystal structure form a large group of solids with interesting electrical and magnetic properties (von Philipsborn, 1974). Naturally occurring thiospinels, although much fewer in number (Vaughan and Craig, 1978), form a diverse group of minerals which exemplify problems of more general interest in sulfide mineralogy. The systematics of the spinel structure-type have recently been reviewed by Hill *et al.* (1979) and further data on the properties, phase relations and crystal chemistry of certain thiospinel minerals are provided by Vaughan and Craig (1978).

Qualitative molecular orbital and band theory models have been applied to gain an understanding of the chemical bonding in thiospinels by Goodenough (1969) and by Vaughan *et al.* (1971). The latter authors also showed how such models may be employed in order to understand the composition limits, variation in cell parameters, microhardness, reflectance properties, relative stabilities and hence geological occurrence of the mineral thiospinels.

Since publication of the qualitative models, methods for the quantitative calculation of molecular orbitals, which give results for transition metal sulfides in good agreement with experimental data from spectra, have become available (Vaughan *et al.*, 1974; Tossell, 1977, for example). In this paper, the results of such quantitative calculations have been used to model the electronic structures of $CuCo_2S_4$ (carrollite), Co_3S_4 (linnaeite) and Fe_3S_4 (greigite). Models derived from the calculations are then compared with the qualitative models and the properties of thiospinel minerals considered in the light of these new models.

Quantitative calculations—methods and results

The Self-Consistent-Field X_α Scattered-Wave Cluster method (abbreviated "SCF-X_α-SW") is a molecular orbital method which yields results in good quantitative agreement with experiment for many chemical and mineralogical systems (Johnson, 1975; Messmer, 1977; Rosch, 1976; Tossell *et al.*, 1974; Vaughan *et al.*, 1974; Tossell, 1978a).

The method is based on the division of a crystalline structure into component polyatomic clusters such as the CoS_4^{-6} tetrahedral unit which can be used to represent the tetrahedral site Co^{2+} in Co_3S_4. The space within and around the cluster is geometrically partitioned into atomic sphere regions cen-

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tered on the metal and anion nuclei, with spheres in contact and completely enclosed within an outer sphere beyond which is an extramolecular region. Within the outer sphere but between atomic sphere regions is the interatomic region. The electrostatic potential of the remaining atoms in the crystal lattice is approximated by a spherical shell of positive charge (the Watson Sphere) passing through the anion nuclei.

The potential energy in the various regions is evaluated using electrostatics together with the X_α statistical approximation of Slater; the potential is then simplified and used to solve numerically the one-electron Schrödinger equation in each region. The resulting wave functions and their first derivatives are joined continuously through the various regions using multiple-scattered-wave theory. From this result, the spatial distribution of electron density is calculated and used to generate a new potential for the next iteration. The entire procedure is then repeated until self-consistency is attained and the result is a set of one-electron molecular orbitals characterized by their energies and electron density distributions.

In this work, calculations on the clusters CuS_4^{-6} (and CuS_4^{-7}) CoS_4^{-6}, CoS_6^{-9} (low-spin Co^{3+}), FeS_4^{-5}, FeS_6^{-10}, FeS_6^{-9} have been employed in constructing one-electron MO models for the three thiospinels. The choice of oxidation state and spin-state for the cation employed in the calculation was based on evidence available from electrical and magnetic studies, neutron diffraction, Mössbauer spectroscopy and electron spectroscopy (see Vaughan and Craig, 1978, for further information).

Although the calculations provide data on the relative energies of all valence and core orbitals, it is only the highest energy orbitals of the valence region which are significant for understanding bonding models and the properties of the sulfides. In these copper, cobalt and iron sulfides, it is orbitals dominantly of metal 3d character which occur at the top of the valence band and influence the properties of the materials. This observation is confirmed by the results of the calculations shown in Figure 1 where only the highest energy filled and lowest energy empty orbitals are illustrated. In this figure, the relative energies of these orbitals derived from calculations on the different clusters are shown with nonbonding sulfur 3p-type orbitals taken as the zero point on the energy scale. (t_{1g} and t_1 orbitals, all orbitals being labelled according to the standard group theory nomenclature for T_d and O_h symmetry groups). For each mineral species, the t_{2g} and e_g orbitals in octahedral coordination and e and t_2 orbitals in tetrahedral coordination are shown and these are the partially occupied (dominantly metal

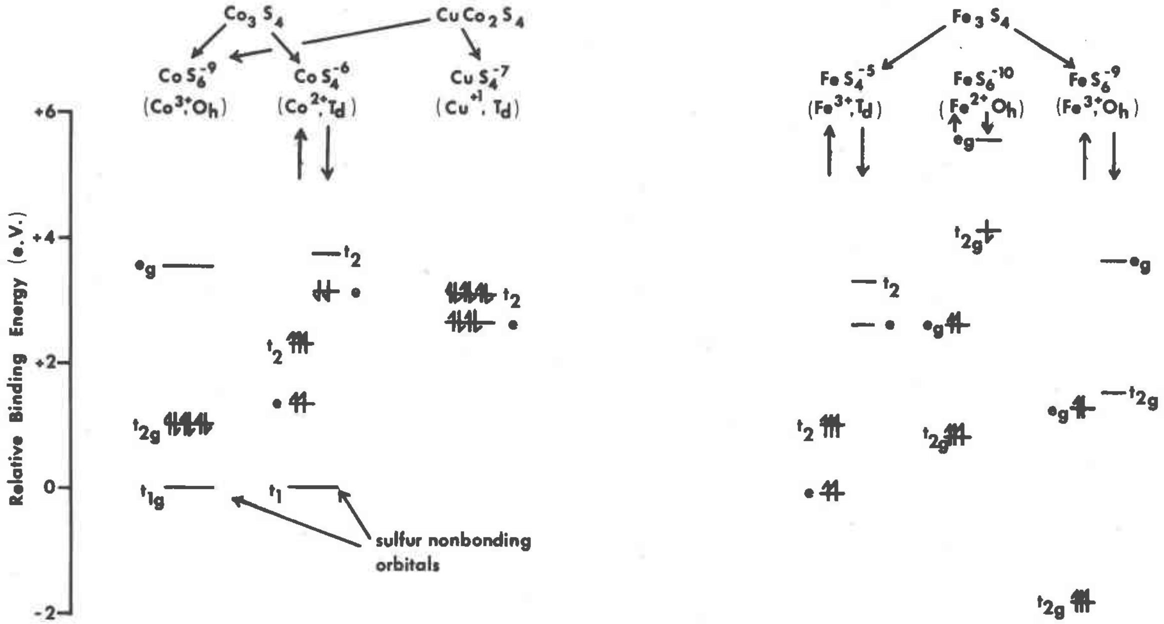

Fig. 1. Orbital energy level diagram showing results of SCF-X_α-SW calculations on the clusters CoS_6^{-9}, CoS_4^{-6}, CuS_4^{-7}, FeS_4^{-5}, FeS_6^{-10} and FeS_6^{-9} for the relative energies of outermost (valence) orbitals. For those systems containing unpaired electrons the effects of spin-splitting into spin-up (↑) and spin-down (↓) MO's is shown.

3d type orbitals) at the top of the valence band. For 3d configurations in which unpaired electrons occur, a further effect to consider is that of spin-splitting of the MO energy levels into spin-up and spin-down sets as shown in Figure 1.

Comparison of quantitative and qualitative approaches

The orbital energy diagrams shown in Figure 1 for CoS_6^{-9} and CoS_4^{-6} indicate that the empty e_g orbitals of the octahedral cluster will be close in energy to the partially filled e orbitals of the tetrahedral cluster. Since the energy of interaction between orbitals varies inversely with their energy difference, we would expect the octahedral site e_g and tetrahedral site e orbitals to mix substantially. A band of energy levels would thus be formed with a width greater than the original e_g–e separation. This will lead to metallic conductivity and weak temperature independent (Pauli) paramagnetism of Co_3S_4. The resulting band energy level diagram will be very similar to those postulated by Goodenough (1969) and Vaughan *et al.* (1971).

In extending in composition to $CuCo_2S_4$, overlap can again be envisaged between empty e_g orbitals on octahedral site cobalt atoms and e and t_2 orbitals of the tetrahedral site copper. Although the assumed oxidation state of copper is Cu^{2+} we have reason to expect from other calculations (Tossell, 1978a) and spectroscopic data (Nakai *et al.*, 1978; Folmer and Jellinek, personal communication) that the oxidation state of copper approaches Cu^{+1}. Again $CuCo_2S_4$ is a metallic Pauli paramagnet and the qualitative orbital diagram proposed on the basis of observed properties (Goodenough, 1969; Vaughan *et al.*, 1971) is supported by the results of calculations. The clusters chosen as approximate models for $CuCo_2S_4$ are CoS_6^{-9} and CuS_4^{-7} for reasons discussed above. Such a set of electron configurations suggests a deficiency of electrons on the S anions. An alternative assumption of a d^5 configuration on octahedral Co would stabilize the t_{2g} orbital so much that it and the Cud^{10} t_2 would no longer be close in energy and would interact only weakly leading to nonmetallic behavior.

Greigite, Fe_3S_4, in contrast to the other two thiospinels, has ferrimagnetic and semiconducting properties and the Mössbauer spectrum suggests high-spin Fe^{3+} in tetrahedral and octahedral sites and high-spin Fe^{2+} in octahedral sites (Vaughan and Ridout, 1970; Hulliger, 1968). The model for the electronic structure of greigite shown in Figure 1 emphasizes the importance of spin-splitting of the orbitals in the valence region. A previous study of Fe_3O_4 (Tossell, 1978b) yielded a qualitatively similar cluster MO diagram. Studies on Fe_3O_4 (see Shuey, 1975) have shown that its conductivity increases greatly above its Verwey temperature (119K), at which the Fe ions in the octahedral site become indistinguishable. In this state, the t_{2g} octahedral site orbital is close in energy to the e tetrahedral site orbital and so strong mixing and metallic conductivity ensues. Such may also be the case for greigite.

Electron structure models and the properties of thiospinels

The qualitative models outlined by Vaughan *et al.* (1971) were used to show how variations in unit cell parameter, microhardness, and reflectance could be explained for the mineral thiospinels in terms of bonding models. In terms of smaller overall unit cell parameters and metallic properties, thiospinels such as Co_3S_4, $CuCo_2S_4$, Ni_3S_4 and $FeNi_2S_4$ are considered to form a group characterized by delocalization of the outermost (essentially metal 3d) electrons. The calculations support this approach to the electronic structure of Co_3S_4 and $CuCo_2S_4$ and give confidence in its application to the other thiospinels. Variations of physical properties and in stabilities of members of this group can be interpreted on the basis of the number of electrons occupying the band formed from the e_g and e orbital overlap.

In contrast to the metallic group of thiospinels, greigite and a number of other minerals including daubréelite show evidence of having localized valence electrons. The unit cell parameters of members of this group are appreciably greater and evidence of stable solid solution series not seen; observations which can be explained on the basis of the major differences in electronic structure observed between members of the two groups and well shown for the case of greigite in Figure 1. Further evidence will be presented elsewhere (Vaughan and Craig, in preparation) to show that greigite is metastable. Examination of Figure 1. suggests that the occupancy of highly destabilized antibonding orbitals by electrons would cause such instability.

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