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PS-16.01.12 QUASI-FREE ELECTRONS AND EXCHANGE INTERACTIONS IN THE SHORT-RANGE ORDER STRUCTURE OF MATERIALS

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From experimental results with ESR in combination with other methods, numerous exchange interaction complexes of odd electrons and the concerning effects in different disordered materials have been revealed. The behaviour of the complex centers shows the following unusual, special characteristics: - The effects appear only under definite structural perturbations of the short-range order in the material, e.g. the local phase transition, the ratio of the distances between the respective atoms; - There are observed regular displacements of ESR line groups to one side of the higher or lower magnetic field strengths; - Often, the ESR spectral intensity concentrates to only individual lines of the group, other lines become very feeble; - In some special cases, a line inversion (i.e., an emission) is plainly observable; - An axial symmetry quasicrystal structure may be revealed, e.g. in some coating thin films and vegetable fibres. It is especially notable that these new effects stand in close connection with the fundamental properties of the material (such as the conductivity, the catalysis, the fastness, etc.), and with the details of a technological nature arising mainly from distinctions in the mode of preparation.

Over a long period of time we have carefully pursued these phenomena and come to the conclusion that they only can be adequately explained through a new consideration on the grounds of the Short-Range Order Structure (SROS). On the basis of the experimental results, a model for Quasi-Free Electrons (QFE) in the Resonant Cavity (RC) constituted by the valence bond planes of the short-range order network and a model for the Super-Exchange Interaction in the SROS of the materials have been elaborated. The sole quantum state of the QFE in the RC only can be a Standing Wave. Therefore, the pair coupling probability depends resonantly on the super-exchange path length between the two respective Spins. The SROS perturbations can produce in the RC a relatively strong local electric field of low symmetry, under the action of which the QFEs can be strongly "polarized", and therefore obtain a considerable energy splitting term. This effect gives rise to the regular displacements of the ESR line groups. In the ground wave states of the QFEs in the SROS, there are only two allowed energy bands. The states of negative effective mass and greater-becoming effective mass of the QFE can persist near the lower band-edge. The population distribution course of QFEs shows a "compression" form with a pitch. These peculiarities spring from the natural reaction of the RC to the broadcloth of energy level to band and from the natural statistical fluctuation of the RC parameter in the SROS, they give rise to some unusual phenomena such ESR emission, sudden conductivity changes, spectral intensity concentration. These effects occur especially distinctly in the case of an excellent short-range ordering or an ideal amorphism in the material. On the basis of these models there is the possibility of a more profound understanding about the appearance and the role of interaction complexes in the SROS of materials, and therefore of the molecular electronic micromechanisms concerning the respective specific features and technological factors of these materials. Numerous application cases have been examined. As illustration examples, the two types of the super-exchange couple pairs [Cu-Y+Cu] corresponding to a degenerated orthorhombic structure and the superconducting mechanism in the $YBa_2Cu_3O_x$ compound,

and the phenomena of the sudden conductivity changes in amorphous silicon are exposed and discussed.

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STRUCTURAL FEATURES OF POTASSIUM AND CESIUM DODECAHYDRO-CLOSO-DODECABORATE ACCORDING TO NMR DATA.

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The X-ray data (Wunderlich J. A., Lipscomb W. N., J. Amer. Chem. Soc., 1960, 82, 4427-4428) show, that the length of chemical bond B-H in the closo-anion $B_{12}H_{12}$ of the salt $K_2B_{12}H_{12}$ is anomalously short (1.07 Å) as compared to the known length of chemical bond in boron hydrides and their derivatives (1.21 Å). The question arises about the reasons, which caused this shortness of the length of chemical bond in $K_2B_{12}H_{12}$. In this work we have made determination of the distance B-H in $K_2B_{12}H_{12}$ and $Cs_2B_{12}H_{12}$ salts by the NMR 1H and ^{11}B method. The determination by this method is possible with the proviso that the high dipole-dipole interaction occurs between the nuclear spins of the boron and hydrogen atoms in the two-spin B-H system. From the analysis of the NMR spectrum shape we have obtained for the length of the B-H chemical bond 1.22 ± 0.02 Å in the investigated samples. Moreover, it has been found that the X-ray data associated with the localization of the atoms of hydrogen do not agree with the characteristic feature of dipole-dipole interaction of protons according to the NMR data. The observed distinctions in the results of the NMR and X-ray methods can be attributed to the occurrence of disorder in the arrangement of hydrogen and boron atoms in the crystalline lattice. It is possible that the nature of this disorder is connected with the fact that the $B_{12}H_{12}$ closo-anion is a regularly shaped icosahedron. The localization of this anion in the crystalline lattice must lead to disordering and quasiperiodicity of the crystal.

PS-16.01.14 New Aspects of the Structure of Nitrogenase and FeMoco using X-ray Absorption (XAS) Techniques

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Experimental methods based on x-ray Absorption Spectroscopy are being further developed which enable new insights to be obtained into the solution structure of FeMoco both within

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and outside of the MoFe protein. Improvements in data collection methods have been coupled with advanced techniques of EXAFS data analysis to provide significantly more information on the structural nature of this cluster. Experimental data has been obtained at the S, Fe, and Mo edge. Analysis of EXAFS data has utilized a new approach based on theoretical parameters and multiple scattering analysis (called GNXAS) to provide more reliable information about longer-range interactions in the polynuclear FeMo cluster. Additional information has been determined about electronic structural changes upon redox chemistry using *in situ* electrochemical control. This work is supported by grants from NIH and NSF. The data were measured at the Stanford Synchrotron Radiation Laboratory which is operated by the U.S. DOE.