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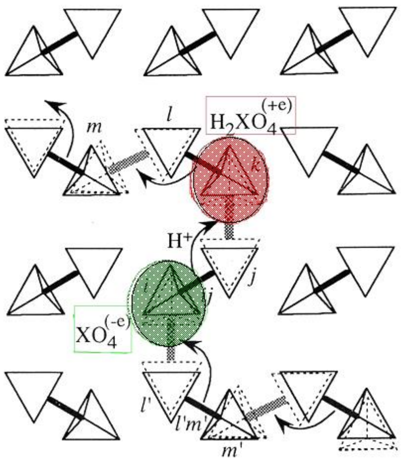
Research on Theory of Superionic Conduction in the Hydrogen-bonded Systems

Abstract

This research has been conducted with collaboration of the experimental group of Professor Seiichiro Ikehata of Dept. of Applied Physics in Tokyo University of Science. Hydrogen-bonded materials, whose nature is closely related to the behavior of protons in hydrogen-bonds, exhibit a number of interesting phenomena. In this context we have recently been working on the mechanism of superionic conduction in $M_3H(XO_4)_2$ [M=K, Rb, Cs and X=S, Se] type dielectric crystals. These materials exhibit a ferroelastic phase transition at high temperature such as 400K, and an anomalously large increase of electrical conductivity has been observed near the phase transition temperature Tc. In this research the mechanism of superionic conduction just below and above Tc has been investigated with collaboration of the experimental group of Professor Seiichiro Ikehata of Dept. of Applied Physics in our university. In the first phase of the present research we have clarified the key features of the conduction mechanism in the high temperature "superionic" phase.



Those are; (1) two kinds of ionic states, $H_2XO_4^{(+e)}$ and $XO_4^{(-e)}$ are formed thermally by breaking of the hydrogen-bonds; (2) $H_2XO_4^{(+e)}$ and $XO_4^{(-e)}$ ionic states move coherently from an XO_4 tetrahedron to a distant XO_4 as the result of successive proton tunneling among the hydrogen bonds. The density of states for the coherent motions of these ionic states calculated by the recursion formula shows the characteristic feature of the Bethe lattice; that is the appearance of the twin peak structure characteristic of one-dimensional coherent paths. The calculated conductivity is very high such as the order of $10^{-2}\,\Omega^{-1}\mathrm{cm}^{-1}$ at Tc, consistent with experimental results. In the present phase of the research the mechanism of conduction below and at the phase transition Tc is investigated. Just below Tc, it is suggested that by the precursor effect of the phase transition, the ferroelastic phase consists of the mixture of superionic regions in which the distances between XO_4 tetrahedrons are the same and of the insulating regions in which XO_4's form XO_4-H-XO_4 dimers by hydrogen-bonds. As a result the superionic region contributes to the ionic conductivity for $T<Tc$ and the development of superionic regions along the electric field leads to the $(Tc-T)^{-1/2}$ power law in the temperature dependence of conductivity just below Tc. From the present result we would like to suggest that the occurrence of the ferroelastic phase is due to the competition between the decrease of kinetic energy by the successive proton tunneling and the increase of elastic energy by the deformation of the hydrogen-bond systems.

References:

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