CHEMISTRY LETTERS, pp. 569-572, 1983. © The Chemical Society of Japan 1983

DIELECTRIC ABSORPTION IN POLYCRYSTALLINE IRON(II) PHOSPHATE. A POSSIBLE MODEL OF ELECTRON HOPPING BETWEEN TWO SITES IN THE CRYSTAL LATTICE

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A remarkable dielectric absorption has been observed in the polycrystalline sample of iron(II) phosphate at room temperature with the maximum of absorption at about 20 Hz. Electron hopping between two sites in the crystal, i.e., between Fe^{2+} and Fe^{3+} ions, is suggested as a possible mechanism of this dielectric absorption.

Iron(II) phosphate, $Fe_3(PO_4)_2\cdot 8H_2O$, the mineral "vivianite", is known to be pleochroic, showing different colours along the three crystal axes, cobalt blue(α), nearly colourless(β) and pale olive-green(γ), respectively,1) while the existence of Fe^{3+} ions of considerable amount has been confirmed by Takashima and Ohashi2) by the measurement of Moessbauer effect, notwithstanding the chemical constitution as an iron(II) phosphate. The crystal structure analysis by Mori and Ito3) reveals that there are two kinds of site for the Fe^{2+} ions in the unit cell, "site 1" and "site 2": the Fe^{2+} ions at the site 2 form a pair of ions of separation, 2.96 Å, along the b axis, while the distance between iron ions at the site 1 and site 2 is 5.24 Å also along the b axis. Although the location of Fe^{3+} ions in the lattice remains undetermined, this substance seems to have a characteristic feature of the so-called mixed-valence compound which has been the subject of recent investigations by a number of workers.4-6) Possible dynamic behaviour of electrons and/or ions in this crystal, as regards the dielectric absorption or electric conduction, has invoked our interest to perform a dielectric measurement at radio- and ultralow frequency region, observing a remarkable absorption at about 20 Hz at room temperature.

Iron(II) phosphate was synthesized in our laboratory from the aqueous solutions of both $FeSO_4$ and Na_2HPO_4, with particular care to avoid presumable oxidation of Fe^{2+} ions at the early stage of reaction. White precipitates produced first changed the colour gradually into dark blue on standing. The sample of the material actually served for the dielectric measurement was the one kept in a sealed flask for almost 10 years after the synthesis. The sample was ground to a fine powder and then made a disk of 40 mm in diametre and 1.41 mm thick under the pressure of 15 tons/cm^2. Dielectric measurements were performed with use of a transformer bridge (ANDO TR-1C), and an ultralow-frequency bridge(ANDO TR-4), together with a three-terminal capacitance condenser as a measuring cell, which was kept in an electrically regulated air thermostat.

One of the results of dielectric absorption, observed at 26.3°C, is shown in Fig. 1 as a Cole-Cole plot, which exhibits clearly that the relaxation process in this crystal is of the Davidson-Cole type with a characteristic distribution of relaxation time,[7] $\varepsilon^* - \varepsilon_\infty = (\varepsilon_\circ - \varepsilon_\infty)/(1+j\omega\tau)^\beta$, where ε^* is the complex permittivity, $\varepsilon_\circ$, ε_∞ are the permittivities at static and extremely high frequency electric field, respectively; ω is the angular frequency, τ the relaxation time, and β is the parametre characterizing the distribution of relaxation time. The following values are obtained for these parametres: $\varepsilon_\circ = 102$, $\varepsilon_\infty = 6.2$, $\varepsilon''_{max} = 33.1$, $f_{max} = 21.9$ Hz, $\tau = 1.22 \times 10^{-2}$ s, $\beta = 0.572$. Here, f_{max} is the frequency at which the absorption reaches the maximum value, $\varepsilon''_{max} = 33.1$.

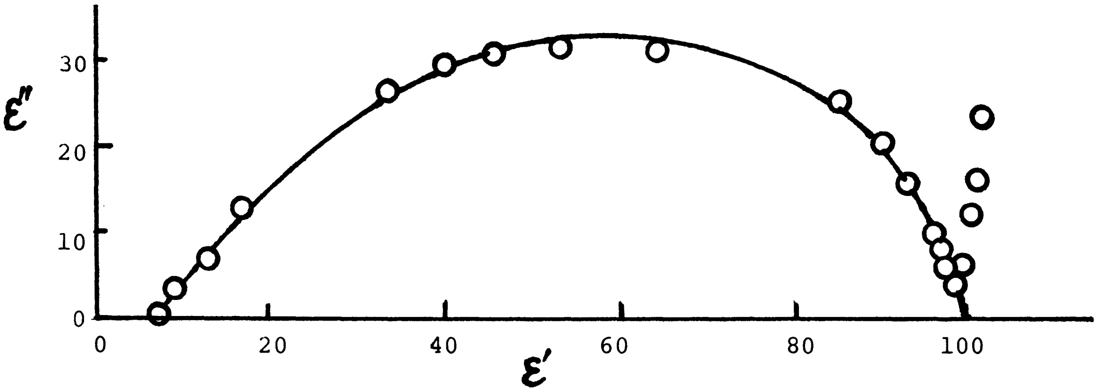

Fig. 1 Cole-Cole plot of the permittivity of iron(II) phosphate (26.5°C).

The Arrhenius plot of log(τ) against reciprocal temperature gives a straight line in the temperature range of 25 to 35°C (Fig. 2), from which the energy of activation for this relaxation process is obtained as $\Delta H = 118$ kJmol^{-1} (28.1 kcal/mol). This value is fairly large compared with those for the reorientational process of usual small molecules in the crystal, such as the water of crystallization,[8] or the phosphate ion. Further, the low value of f_{max}, 21.9 Hz, too, suggests a mechanism other than the molecular reorientation for this dielectric absorption: accoding to Ref. 8, f_{max} for the relaxation process of the water of crystallization is usually found around 10^3 Hz.

The hopping of electrons between two sites localized in the crystal lattice or in the non-crystalline solids has been proposed recently as the cause of dielectric absorption at low frequencies, in some of the charge-transfer complexes[4] and in a mixed-valece salt, $K_3(MnO_4)_2$.[5] Lewis has discussed these phenomena theoretically.[9] Thus, we might apply this hopping model to the dielectric absorption observed in $Fe_3(PO_4)_2 \cdot 8H_2O$ as follows: first, let us admit that there are a considerable amount of Fe^{3+} ions occupying either site 1 or 2, instead of Fe^{2+} ions, as suggested by Takashima and Ohashi of some vivianites before[2] (the ratio of Fe^{3+} to Fe^{2+} amounts to almost 1, sometimes). The oxidation of Fe^{2+} ions may be due to the contact with air, presumably reinforced by the electron-withdrawing tendency of the $(PO_4)^{3-}$ ion, as was pointed out by May[10] and also by Van der Lugt and Poulis[11] on the basis of the observed chemical shift in ^{31}P nuclear magnetic resonance spectrum of vivianite. The formation of a charge-transfer bond between Fe^{2+} and $(PO_4)^{3-}$ ions might be expected like $[Fe^{2+}]^+ \cdot [(PO_4)^{3-}]^-$, where Fe^{2+} is the donor D and $(PO_4)^{3-}$ is the acceptor A, in the usual notation.

On the other hand, the bonding between Fe^{2+} and $(PO_4)^{3-}$ must be through oxygen atoms of the phosphate ion, the Fe^{2+} at the site 1 being coordinated by two oxygen atoms, while those at the site 2 being coordinated by six oxygen atoms of phosphate ions, which form a double octahedral group of oxygen.[3)] As each Fe^{2+} ion of the pair(site 2) should have equal probability of forming a charge-transfer bond with $(PO_4)^{3-}$ ion, $D^{+}\cdot A^{-}$, the alternation of this bonding would occur between Fe^{2+} and the phosphate ion concerned with an appropriate time constant, which would result the reorientation of an effective dipole of rather large moment (4.80x2.96= 14.2 Debye[47.4×10^{-30} Cm], at least). This reorientation of dipole could give rise to a large dielectric absorption if electric field of appropriate frequency is applied. Figure 3 shows schematically the relation between the donor and acceptor with the transfer of an electron between Fe^{2+} and Fe^{3+} ions separated by a potential barrier. The distances, r_i, r_j and r_{ij} are approximately 2.0 Å for the former two and 2.96 or 5.24 Å for the latter, respectively.[3)]

The arrangement of ions in the lattice of vivianite is partly shown in Fig. 4, drawn using the crystal data from Ref. 3; the location of the molecules of the water of crystallization is omitted which are known to be arranged in such a way that every four of them form a tetrahedron bonded to each other by weak hydrogen bonds along the ac plane (cleavage plane). As can be seen from the figure, there are a number of ways conceivable through which the electron could be transferred from Fe^{2+} to Fe^{3+}, such as Fe^{2+}-O- Fe^{3+}, Fe^{2+}-O-P-O- Fe^{3+}, etc., other than the direct transfer from Fe^{2+}(site 2) to Fe^{3+}(site 2). These multiple paths of electron transfer could be the origin of the distribution of relaxation time characteristic of the Davidson-Cole type, depending on the magnitude of the potential barrier for the respective electron transfer. Still, quantitative estimation of the relaxation time for the respective process mentioned above is difficult at the present stage and left for the future investigation.

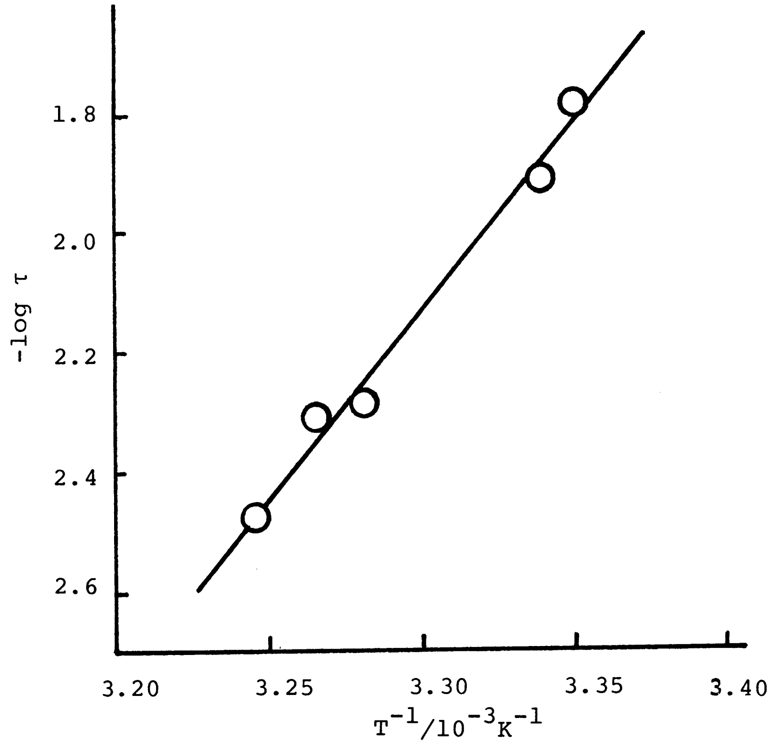

Fig. 2 Arrhenius plot of log τ vs. T^{-1}.

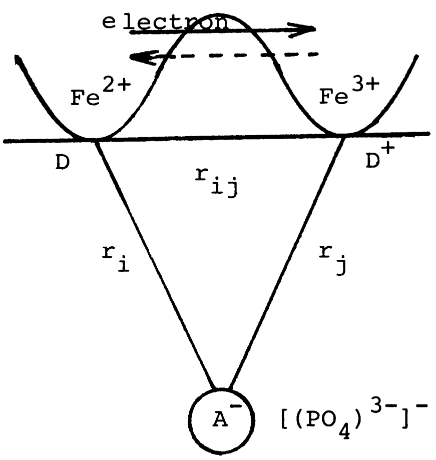

Fig. 3 Relation between donor D and acceptor A, and the site for Fe ions separated by a potential barrier.

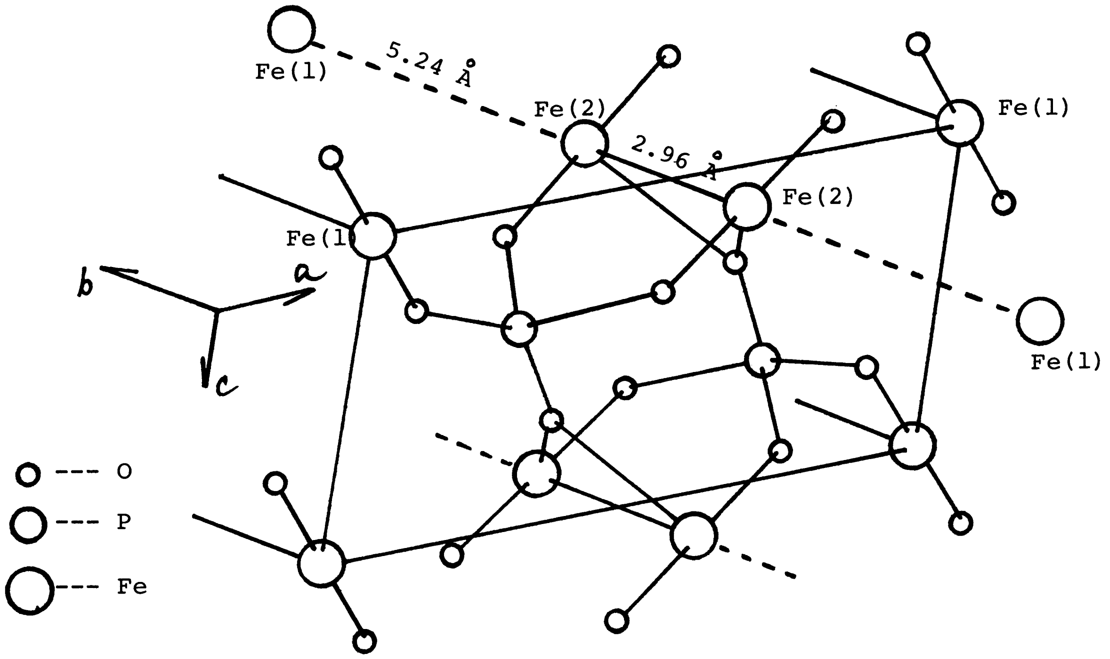

Fig. 4 Arrangement of ions along ac plane of vivianite(schematic).

The authors are grateful to Hiroshi Kuroda and Shuji Maeda for their help in dielectric measurements and also to Drs. Fujiko Iwasaki and Shigeo Hayashi for the stimulating discussions.

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(Received January 26, 1983)