MARCUS RATE-EQUILIBRIUM THEORY.

PS11.03.09 CRYSTALLOGRAPHY AND KINETICS: STRUCTURE CORRELATIONS IN THE LIGHT OF MARCUS RATE-EQUILIBRIUM THEORY. Valeria Ferretti, Paola Gilli, Valerio Bertolasi and Gastone Gilli, Dipartimento di Chimica and Centro di Strutturistica Diffrattometrica, Università di Ferrara, via L. Borsari 46, 1-44100 Ferrara, Italy

Systematic comparison of crystal structures containing the same molecular fragment leads to structure correlations, that is intercorrelations of fragment geometrical parameters in its configuration space. Structure correlations are supposed to map minimum-energy pathways in the fragment PES (Potential Energy Surface) (Dunitz, "X-ray Analysis and the Structure of Organic Molecules", Cornell, Ithaca, 1979; Bürgi & Dunitz, Acc. Chem. Res. 1983, 16, 153).

The exact relationship between crystal structure correlations and chemical kinetics (or chemical equilibrium) is a complex physical-chemical problem which has been seldom treated (see, for instance, Bürgi in "Perspectives in Coordination Chemistry", VCH, Basel, 1992; Ferretti, Gilli, Bertolasi & Gilli, Cryst. Rev. 1996, in press). In this communication an interpretation is attempted which makes use of the Marcus rate-equilibrium theory (Marcus, Discuss. Faraday Soc. 1960, 29, 21; J. Phys. Chem. 1968, 72, 891) to relate crystal structure correlations with the kinetic concepts of activation energy barriers, reaction pathways and distances of the reactants from the transition state as well as with thermodynamic standard free energies of chemical reactions.

PS11.03.10 INFLUENCE OF DOPING ON LOW-FREQUENCY DIELECTRIC RELAXATION OF (VDF-TrFe) COPOLYMER. T.B.Frolova, N.D.Gavrilova, K.A.Verkhovskaya, Moscow State University, Moscow, Russia, Institute of Crystallography RAS, Moscow, Russia

In this paper low-frequency dielectric relaxation of (VDF-TrFe) 70/30, pure and doped with rododine R6G, in frequency range 20Hz-20kHz and temperature region 80-400K were investigated. The region of 310K for the pure copolymer is the region of anomalies of dielectric permittivity and other electrophysical properties. We connect the existence of these anomalies with the structural changes in the amorphous phase of copolymer. After doping by R6G the region of anomalous behavior shifts to 100-110K. Besides, doping results in increasing of values of dielectric permittivity of copolymer (from 80 to 400). The results are used to test the "universal law" of dielectric response.

1. K.A. Verkhovskaya, N.D. Gavrilova, T.B. Frolova, I.A. Smirnova "Low-frequency dielectric dispersion and pyroeffect in ferroelectric copolymer of vinylidene fluoride with trifluoroethylene at phase transitions"/Rev. RAN (ser.phys.)- in printing.
