Energy Migration in the Radiolysis of Solids†

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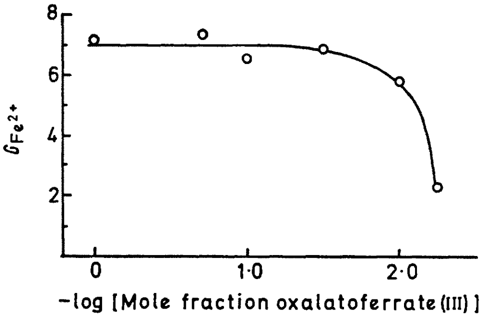
Summary Energy migration, leading to radiolytic decomposition, can be investigated by measuring the number of molecules of a solute decomposed per unit energy deposited in the crystals, as a function of dilution, using isomorphously-incorporated mixed crystals.

SEVERAL mechanisms are known whereby excitation can migrate in a solid, especially a polar solid.[1] Energy transfer, leading to chemical changes, has been studied extensively in organic crystals and glasses,[2] but little has been reported on inorganic systems. Our recent study of the macroscopic radiolysis of some transition-metal oxalato-complexes[3] suggested a very convenient method to study such energy transfer. It is known that salts of the trisoxalatoaluminate anion are comparatively resistant to radiolytic decomposition[4] and that they are isomorphous with the much more radiolytically sensitive trisoxalato-ferrate(III) -cobaltate(III) and -manganate(III) salts.[5]

Thus a study of the radiolysis of solid solutions of the transition-metal complex in a matrix of the trisoxalatoaluminate should reveal the extent of energy transfer. The number of transition metal anions decomposed per 100 ev of energy deposited by ^{60}Co γ-radiation in the mixed crystals has been measured as a function of the mole fraction of transition metal complex in the crystals.

Some data for oxalatoferrate(III) mixed crystals, irradiated at room temperature, are shown in the Figure. These data suggest that energy transfer to the ferrioxalate can take place very efficiently over up to five or six lattice units (*ca.* 60 Å). It is not yet possible to decide whether an electronic or exciton mechanism is involved, although the high *G* values make the former less likely.



FIGURE

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[2] See *e.g.*, J. E. Willard in "Fundamental Processes in Radiation Chemistry," ed. P. Ausloos, Interscience, New York, 1968, p. 599.
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