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This Week's Citation Classic

Castner T G & Känzig W. The electronic structure of *V*-centers.
J. Phys. Chem. Solids 3:178-95, 1957.
[Dept. Physics, Univ. Illinois, Urbana, IL and General Electric Res. Lab., Schenectady, NY]

X-irradiation of alkali halides near 77 K produces halogen$_2^-$ (X_2^-) ions oriented along [110] crystal axes as inferred from ESR data. Detailed analysis and experiments with Tl-doped potassium halides suggest the X_2^- ion is not associated with other imperfections and can be regarded as a self-trapped hole. [The *SCI*® indicates that this paper has been cited over 310 times since 1961.]

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"In recalling the circumstances leading to the discovery of a new color center, the self-trapped hole, we note that the review article on color centers by Seitz[1] had just appeared. Its message was clear: the microscopic structure of most color centers and their mechanism of production by ionizing radiation were speculative.

"We were both at the University of Illinois: Känzig as a research assistant professor (1953-1955) in R.J. Maurer's group and Castner as a graduate student on the verge of starting research in C.P. Slichter's magnetic resonance group. Through Känzig's contact with Slichter's group he decided near the end of his first year in Urbana to study color centers by electron spin resonance rather than by optical methods. With expert advice from several members of the physics department and its excellent resources, he was able to quickly construct a simple, sensitive EPR-spectrometer. The original intent was to study U_2-centers (thought to be impurity H-atoms). Känzig annealed KCl crystals in an H_2 atmosphere, then irradiated them with X rays *in situ* in his EPR cryostat close to 77 K. He found not only the U_2-center EPR spectrum but a beautiful multiline hyperfine spectrum. Slichter suggested it was the hyperfine spectrum of a Cl_2^- molecular ion, namely, a trapped hole or V-center. Upon warming, the EPR-spectrum disappeared irreversibly near the temperature range where the optical V_1-band faded. Känzig thought he had found the EPR of the V_1-center. This identification proved to be wrong. A new color center, the first to be discovered by EPR, had been found.

"Castner was scheduled to work at Los Alamos during the summer of 1955. A tardy Q-clearance resulted in his remaining at Urbana to assist Känzig and to help in interpreting the data. His principal problem, after learning about spin-Hamiltonians, was to simultaneously explain the angular dependence of the hyperfine interaction tensor and the g-tensor. A detailed analysis showed the unpaired hole wave functions of the Cl_2^- ions were *precisely* aligned along [110] axes. The data were inconsistent with a single alkali vacancy neighboring the Cl_2^-. There could either be no neighboring vacancies or two symmetrically positioned vacancies. However; irradiation of KCl:Tl showed a greatly enhanced production rate of Cl_2^- (Tl^+ provided electron traps), thus strongly supporting the no vacancy model. Meanwhile, Känzig was obtaining data for NaCl, KBr, and LiF and continuing experiments at the General Electric Research Laboratory commencing in the fall of 1955. Subsequent optical studies[2] by the Argonne group identified the optical absorption bands of the new V-center—bands slightly shifted from the V_1-bands. The new center was a self-trapped hole (or V_k-center), a fundamental new color center.

"The frequent citing of this work apparently relates to the importance of the self-trapped hole as the fundamental hole-type center and to the hitherto unrealized importance of the formation of X_2^- ions for all types of hole centers. The hole trapping resulted from the formation of X_2^- complexes with their large lattice distortions rather than from polaronic effects. The large number of later studies of the various hole-type centers by EPR and ENDOR, not only in the alkali halides, but in other ionic crystals, certainly helped increase the number of citations."

1. **Seitz F.** Color centers in alkali halides II. *Rev. Mod. Phys.* 26:7-94, 1954.
2. **Delbecq C J, Smaller B & Yuster P H.** Optical absorption of Cl_2^- molecule-ions in irradiated potassium chloride. *Phys. Rev.* 111:1235-40, 1958.