

MASSACHUSETTS INSTITUTE OF TECHNOLOGY

3.014 Materials Laboratory
Fall 2006

Experiment 3: Modules α_1 **F-CENTER ELECTRON QUANTIZATION IN ALKALI HALIDE CRYSTALS***Background*

Alkali halides and alkaline earth halides are strongly ionic compounds that solidify as crystals. The name for the alkali elements (Li, Na, K, Rb and Cs) comes from the Arabic word *alqili* (ashes of the salt-wort plant that was once used as a source of sodium and potassium for making glass from sand). The name for the halogen elements (F, Cl, Br, I—and the rare radioactive element astatine) comes from the Greek word *halos* (ocean) that recalls their dissolved presence (as ions) in seawater. Most alkali halides (LiF through CsF; see Table 1) crystallize in the face-centered cubic rocksalt structure with monovalent ions (cations, anions) having well-defined ion radii (Table 2). Because of cation/anion radius-ratio packing issues, CsCl, CsBr and CsI instead crystallize in the simple-cubic CsCl structure. The alkaline earth fluorides CaF₂, SrF₂ and BaF₂ crystallize in the cubic fluorite structure. Ionic radii depend somewhat on coordination. In the rocksalt structure, each ion is 6-coordinated by ions of the opposite charge; in the CsCl structure each ion is 4-coordinated by its opposite ion. Cations in the fluorite structure are 8-coordinated by anions; anions are 4-coordinated by cations.

A notable feature of these solids is that they are transparent to electromagnetic radiation with wavelengths extending from the far infrared to the far ultraviolet, and they are thus frequently used for optical windows and lenses, particularly in infrared applications where silicate glasses are not transparent. They have similar refractive indices for visible light ($n_{\text{LiF}} = 1.39$, $n_{\text{NaCl}} = 1.50$, $n_{\text{KCl}} = 1.49$, $n_{\text{KBr}} = 1.56$) to those of the silicate glasses ($n \approx 1.5$) more traditionally used for lenses in the visible portion of the electromagnetic spectrum. Their transparency derives from a large band-gap (6-8 eV) between the highest filled states of the valence band (associated with the halogen ions) and the lowest (and unfilled) states of the conduction band (constructed from the empty s-orbitals of the alkali ions).

Table 1. Crystal Data for Alkali and Alkaline Earth Halides

Compound	Lattice parameter, a	Compound	Lattice parameter, a
<i>Rocksalt structure</i>		<i>CsCl structure</i>	
LiF	0.4017 nm	CsCl	0.4110 nm
LiCl	0.513	CsBr	0.4287
LiBr	0.549	CsI	0.4562
LiI	0.600		
NaF	0.462	<i>Fluorite Structure</i>	
NaCl	0.5628	CaF ₂	0.5451
NaBr	0.596	SrF ₂	0.578
NaI	0.646	BaF ₂	0.6184
KF	0.533		
KCl	0.628		
KBr	0.6578		
KI	0.7052		
RbF	0.563		
RbCl	0.6571		
RbBr	0.6868		
RbI	0.7325		
CsF	0.601		

Source: X-ray Powder Diffraction File (International Centre for X-ray Diffraction, 2005)

Table 2. Ionic Radii

Ion	4-coordinated, nm	6-coordinated, nm	8-coordinated, nm
Li ⁺	0.073	0.090	0.106
Na ⁺	0.113	0.116	0.132
K ⁺	0.151	0.152	0.165
Rb ⁺		0.166	0.175
Cs ⁺		0.167	0.181
F ⁻	0.117	0.119	
Cl ⁻		0.167	
Br ⁻		0.182	
I ⁻		0.206	
Ca ²⁺		0.114	0.126
Sr ²⁺		0.132	0.140
Ba ²⁺		0.149	0.156

Source: R.D. Shannon and C.T. Prewitt, *Acta Cryst.*, 1970, **B26**, 1046

Traditional chemistry would normally regard these highly ionic compounds as having stoichiometric compositions, deriving from the ion valencies, but this is not necessarily the case. Deviations from stoichiometry are a consequence of chemical equilibrium and the possibility of defects occurring in the crystal structure. In an NaCl crystal, for example, a Na⁺ cation and a Cl⁻ anion could be removed from the interior and placed on the surface, expanding the crystal and leaving behind in the interior a missing Na⁺ ion (a cation vacancy, V_{Na}) and a missing Cl⁻ ion (an anion vacancy, V_{Cl}). There is an energy cost to form such vacancy defects (called the vacancy formation enthalpy h_V^f , ≈ 1 eV = 1.6×10^{-19} J per vacancy in NaCl), but the entropy of the crystal is correspondingly increased with the addition of the defects, and the free energy of the system is consequently lowered from this competition between enthalpy and entropy. Vacancy defects are known as Schottky defects, and the (stoichiometric) pair of defects—a cation and an anion vacancy—formed in this example is called a Schottky pair. The equilibrium concentration c_S of such defects depends on temperature

$$c_S = c_0 \exp(-h_S^f/k_B T) \quad (1)$$

where the formation enthalpy h_S^f is for formation of the Schottky pair of defects (the sum of the cation and anion vacancy formation enthalpies, about twice that for either vacancy or about 2 eV in NaCl), and c_0 (~ 150 for vacancies in NaCl) is an entropic factor mostly governed by changes in the vibrational behavior of the ions surrounding the vacancies. The concentration of such equilibrium defects is not large, ~ 1 ppm at room temperature in NaCl, about 1 ppt at its melting point of 801 °C.

If a NaCl crystal is exposed to sodium vapor (partial pressure p_{Na}), Na atoms can dissolve into the crystal to occupy the equilibrium Na vacancies, with the release of an electron as the Na atom converts to a Na⁺ ion. Their dissolution leaves an excess of Cl vacancies and thus a non-stoichiometric composition Na_{1+ δ} Cl. The overall reaction chemistry can be expressed as



The ', \bullet and \times superscripts in eqn. (2) represent the electronic charges associated with the various species, *with respect to the NaCl crystal*. A vacant Na site (V_{Na}') in the crystal is negatively ($'$) charged because the site is surrounded by Cl⁻ ions uncompensated by the single positive charge that would normally be there but is absent; similarly a Cl vacancy (V_{Cl}^{\bullet}) is positively (\bullet) charged. A Na⁺ ion sitting on a Na site ($\text{Na}_{\text{Na}}^{\times}$) in the crystal is neutral (\times) with respect to what the crystal expects at that site. The non-stoichiometry δ (and hence the excess concentration of V_{Cl} over V_{Na}) is related to the Na partial pressure p_{Na} by

$$p_{\text{Na}}/p_{\text{Na}}^{\circ} = (1/c_S^{\circ}) \{ \delta + (\delta^2 + 4c_S^{\circ})^{1/2} \} \quad (3)$$

or

$$p_{\text{Na}}/p_{\text{Na}}^{\circ} \approx \delta/c_S^{\circ} \quad \text{for } \delta \gg c_S^{\circ},$$

where c_S° is the equilibrium concentration of Schottky vacancies at the temperature of Na addition in the absence of Na vapor, and p_{Na}° is the vapor pressure of Na in equilibrium with a NaCl crystal at that temperature. Stoichiometry is thus seen to be a special case, and the ability to deviate from the stoichiometric composition to depend on the ease with which defects can be created in the crystal structure.

If a small amount of Na metal and a crystal of NaCl are placed inside a sealed tube and heated, the Na vapor pressure will rise (to $p_{Na} \approx 0.13$ atm at 700°C) way above the equilibrium partial pressure of Na in the tube if the Na metal had not been added, and excess Cl vacancies and electrons will be generated (about 100 ppm under these conditions). Since the V_{Cl}^\bullet and e' defects are oppositely charged, they attract and the electron can become trapped in the Cl vacancy to form a neutral Cl vacancy



Such a neutral anion vacancy is called an *F*-center. The “*F*” comes from the German word *Farbe* (color), because crystals containing *F*-centers are colored (NaCl is yellow, for example; KBr is blue, *etc.*). An *F*-center, comprising an electron trapped inside a singly positively-charged vacancy, represents an interesting quantized system, not unlike a hydrogen atom which is an electron trapped in the positive potential of a proton. Just as in a hydrogen atom, the electron can occupy a set of hierarchical quantized states ($1s^1$, $2s^1$, *etc.*). The color of an otherwise transparent crystal containing *F*-centers derives from the absorption of visible light at a certain wavelength λ by excitation of the trapped electron from its ground state to its first excited state, representing an energy difference $\Delta U = h\nu$ of a few eV corresponding to visible wavelengths $\lambda = c/\nu = hc/\Delta U$, where $c = 3.00 \times 10^8$ m/s is the speed of light and $h = 6.63 \times 10^{-34}$ J s is Planck’s constant. The hydrogenic electron energy levels U can be obtained by solving the second-order partial differential wave equation, first formulated by Erwin Schrödinger in 1905,

$$U\psi = \{-(\hbar^2/8\pi^2 m_e) [\partial^2/\partial x^2 + \partial^2/\partial y^2 + \partial^2/\partial z^2 + V]\} \psi \quad (5)$$

for the wave amplitudes ψ of an electron of mass m_e ($m_e = 9.1 \times 10^{-31}$ kg) and charge $-1e$ ($e = 1.6 \times 10^{-19}$ C) subjected to the Coulomb potential V of a proton nucleus of charge $+1e$. The corresponding solution for the electron energy yields a series of discrete bound-electron levels

$$U_n = -e^4 m_e / 8\epsilon_0^2 n^2 \hbar^2 \approx -13.6/n^2 \text{ eV} \quad (6)$$

for $n = 1, 2, 3, \dots$ an integer (the “principal quantum number”) and ϵ_0 the permittivity of vacuum. These yield a ground state ($n = 1$) \rightarrow first excited-state ($n = 2$) transition energy

$$\Delta U = U_2 - U_1 = (1/1^2 - 1/2^2) e^4 m_e / (8\epsilon_0^2 n^2 \hbar^2) \quad (7)$$

$$\approx 4.53 \text{ eV for NaCl, or } \lambda_{\text{abs}} = 273 \text{ nm}$$

that only poorly approximates the observed F-center absorption ($\Delta U \approx 2.69$ eV, $\lambda_{\text{abs}} \approx 460$ nm for NaCl), even with ε_0 corrected by the high-frequency dielectric constant ε (= 2.25 for NaCl) of the crystal.

A better model is the “particle-in-a-box,” the electron confined within a three-dimensional infinite potential well of width d given by the dimension of the halogen vacancy. Solving the Schrödinger equation (5) for the infinite potential well yields

$$U = (\hbar^2/8m_e d^2)(n_1^2 + n_2^2 + n_3^2) \quad (8)$$

for n_1, n_2, n_3 integers (quantum numbers), and

$$\Delta U = U_{211} - U_{111} = 3\hbar^2/(8m_e d^2), \quad (9)$$

giving

$$\lambda_{\text{abs}} = \hbar c/\Delta U = (8m_e c/3\hbar) d^2, \quad (10)$$

$$\text{or } \lambda_{\text{abs}}(\text{nm}) = 1098 d(\text{nm})^2.$$

A reasonable estimate for d extends out to the center of the alkali ions surrounding the halogen vacancy, which choice gives $d \approx a$ (a = lattice parameter of the cubic unit cell) for rocksalt- and CsCl-structure alkali halides, and $d \approx a/2$ for the fluorite-structure alkaline-earth fluorides. Hence, a plot of the λ_{abs} against a^2 ought to yield a straight line, and the F-center absorption wavelength should scale with the square of the lattice parameter (known as the “Mollwo¹-Ivey² relation”). The estimate (10) yields $\lambda_{\text{abs}} = 348$ nm for $d \approx a$ in NaCl, lower than the experimental result. In reality, the wave function ψ of the F-center electron extends over rather more of the surrounding alkali ion than is formally contained within the unit cell. Extending d out to the extreme edge of the alkali ion shell, $d \approx a + 2r_{\text{Na}^+}$, yields $\lambda_{\text{abs}} = 628$ nm, nicely bracketing the observed F-center absorption ($\lambda_{\text{F}} = 460$ nm).

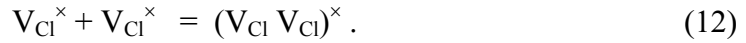
The number of F centers absorbing can be calculated from the amount of light absorbed. The light absorption can be expressed as an absorption coefficient $\alpha(\lambda)$ (expressed in units of m^{-1}); $\alpha = 1$ means that light of that wavelength is completely absorbed in a thickness of 1 m. The related density of F centers is calculable using the formula derived in 1930 by former MIT Professor Olexsander Smakula (1900-83)

$$N_{\text{F}} f = 0.87 \times 10^{21} [n_c/(n_c^2 + 2)] \alpha_{\text{max}} W(\text{eV}), \quad (11)$$

where N_{F} is the density of F centers (m^{-3}), n_c is the refractive index of the host crystal, α_{max} is the absorption coefficient (m^{-1}) at the absorption peak maximum, and W is the width of the absorption peak measured in electron-volts. The factor $f \approx 1$ (0.81 for NaCl, 0.90 for KCl, 0.80 for KBr) is called the *oscillator strength* of the absorbing center and is a measure of the probability of the optically-induced electron excitation. The F -center energy state lies typically in the upper half of the host crystal bandgap, with its first excited electron state very close to (and higher excitation states degenerate with) the

conduction band. The trapped electrons excited above their ground states are therefore susceptible to further thermally-induced excitation ($\Delta U \approx k_B T \approx 0.02$ eV at room temperature) at non-negligible rates into the conduction band, whereupon they are lost from the F -centers. Hence, crystals containing F centers need to be kept in the dark or they will lose their color (the loss is referred to as “bleaching”).

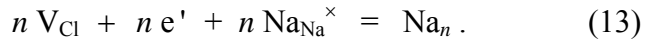
Small elastic distortion fields accompany F -center vacancies, arising from the relaxation of ions around the vacancy, and these are sufficient to provide a driving force for F -centers to aggregate (at temperatures sufficiently high that there is some ion mobility). The first step is the dimerization reaction (illustrated here for a chloride)



¹E. Mollwo, *Göttingen Nachr.* **97** (1931) 236. ²H. F. Ivey, *Phys. Rev.* **72** (1947) 341.

The di- F -center in (12), sometimes written F_2 , is a pair of nearest-neighbor halogen vacancies (oriented along $\langle 110 \rangle$ in rocksalt structure and fluorite structures and along $\langle 100 \rangle$ in CsCl structure) that have trapped *two* electrons. This center (for historical reasons called an M -center) is the analogue of a He atom and comprises *two* electrons in a (somewhat extended and odd-shaped) box. Because one electron partially screens the positive charge for the second, the first excited electron state is lower in energy than that of the F -center, and the M -band absorption occurs at longer wavelengths.

Continuing the aggregation process (for example by annealing the crystal) yields large aggregates of F -centers. Such an aggregate contains positively-charged alkali ions, trapped electrons, and no halogen ions. At some point, the trapped electrons will become completely associated with the cluster of n isolated alkali ions, entering the conduction band of what then becomes a (neutral) alkali metal inclusion of nanometer dimensions,



Color-center physicists were, in fact, investigating the properties of these nanoparticles in the 1930's, 50 years before that buzzword entered the popular technological lexicon. Curiously, electron diffraction studies have shown that the alkali metal atoms retain the fcc positions of their alkali ion precursors in rocksalt-structure halides, rather than adopting the bcc positions found in bulk alkali metals, which have bcc structure. These metallic inclusions can reach dimensions approaching colloidal size (tens to hundreds of nm) and thus scatter light. Because they nucleate heterogeneously at sites of lower local density, such as at the cores of dislocations, their light-scattering was employed in the 1950's to visualize dislocations in transparent alkali halide crystals at a time when the existence of dislocations was still doubted by some scientists. These metallic particles are associated with a broad absorption band, at even longer wavelengths than the F_2 absorption band, that is attributable to a combination of light scattering (whose wavelength dependence depends on particle size) and a *collective* (jello-like) excitation of the quasi-free conduction-band electrons of the metal, called a *plasmon* resonance. The excitation energy associated with the latter is given by

$$U_{\text{pl}} = h \nu_{\text{pl}} = h (\rho_e e^2 / \pi m_e)^{1/2} , \quad (14)$$

where ρ_e is the free-electron density of the alkali metal. For Na, there is one free electron per Na atom, so $\rho_e = \rho_{\text{Na}} = 2.5 \times 10^{28} \text{ m}^{-3}$ and $U_{\text{pl}} \approx 5 \text{ eV}$. The corresponding absorption band maximum for a crystal of refractive index n_c is

$$\lambda_{\text{abs}} = hc(1 + 2n_c)^{1/2} / U_{\text{pl}} = [\pi m_e c^2 (1 + 2n_c) / \rho_e e^2]^{1/2} \quad (15)$$

which falls in the red part of the optical spectrum for NaCl; hence NaCl containing a high density of colloidal Na will appear blue in transmission.

Chemically-driven non-stoichiometry is not the only way to produce F-centers. Radiation is another. Irradiating with any form of ionizing radiation, such as electromagnetic radiation in the spectrum from ultraviolet light ($U > 6 \text{ eV}$) through X-rays

($U \sim \text{keV}$) to gamma rays ($U \sim \text{MeV}$) or energetic charged particles (such as electrons or ions in the $U \sim \text{keV}$ to MeV range) generates free electrons in an ionic solid that are easily trapped in any existing anion vacancies. The concentration of the latter, however, is very diminishingly small, except near the melting point, unless anion vacancies have been introduced chemically or by some other means. (A short irradiation with UV light or X -rays is, in fact, a good way to repopulate F -centers with electrons when they have been bleached by extensive exposure to light.) Radiation has the additional capacity, though, to knock atoms around in a solid and off their normal atom sites, hence *creating* the vacancies themselves. This is clearly feasible for *particle* irradiation, where billiard-ball-like collisions of particles with mass m and kinetic energy T with atoms of mass M can transfer kinetic energy to the struck atom up to a maximum energy transfer

$$T'_{\max} \leq [4mM/(M+m)^2] T. \quad (16)$$

It takes kinetic energies typically about 3-4 times the cohesive energy of the solid to remove an atom from its atom site and stuff it into some other place (typically an interstice); for Na^+ and Cl^- ions in NaCl , this displacement energy is about 25 eV. Such energies are easily transferred by fast neutrons ($T \sim 1 \text{ MeV}$) from a nuclear reactor or by incident ions ($T \sim 50 \text{ keV}$) during ion implantation of a solid. Much lighter electrons (of mass $m_e \ll M_{\text{Na}}$ or M_{Cl}) must be accelerated to kinetic energies $T \sim 250 \text{ keV}$ (at that point traveling with about 80% the speed of light) to have sufficient energy to effect the atom displacements.

In halides, additionally (in common with a number of other solids, such as hydrides, silicates and all organic solids), an efficient atom displacement mechanism exists for removing atoms from their sites using *only ionizing* radiation, such as UV light, X -rays or γ -rays. This process is called *radiolysis* and in halides can be surprisingly efficient (up to $\sim 50\%$ of the ionizing energy converted to kinetic energy in displacing a halogen atom from its site).

Without going into elaborate detail, the mechanism involves excitation of valence (least tightly bound) electrons by the ionizing radiation. In halides, the valence electrons are those associated with the halogen anions (lodged in $2p^8$ -like orbitals around Cl^- ions, for example, whereas all the $3s^1$ electrons have been removed from Na atoms in making them Na^+ ions). An X^- halogen ion with one of its valence electrons excited into the conduction band dominated by the M^+ alkali ions in an MX halide has trapped a hole (absence of an electron) to become something resembling a neutral atom that is unstable in its halogen ion site; it moves off-center and binds to a neighboring halogen ion, forming an X_2^- molecular ion occupying an adjacent site and leaving behind a halogen vacancy (with an associated excited electron). The latter is just an F -center, while the former (called an H -center for historical reasons) migrates quickly away, reacts with another H -center and forms interstitial X_2 halogen molecular defects which have their own spectroscopic signature in the violet portion of the light spectrum (and hence are called V -centers). Because of the efficiency of the process, a few minutes or hours in the beam of an X -ray tube is sufficient to produce a sizable population of F centers ($c_F \approx 100$

ppm). F_2 -centers are also produced, either statistically or if the F -centers produced have enough thermal mobility to find each other.

This mechanism of coloration was in fact extensively exploited during World War II in so-called “dark trace” cathode-ray tubes used to image radar scans used before long-persistence phosphors and or digital imaging were developed. In these, an electron beam was steered to a screen coated with powdered alkali halide (usually KCl), which accumulated light-absorbing F -centers under the ionizing electron beam. Exposure of the screen to bright light or heat was sufficient to bleach the F -centers produced and so “erase” the screen for a subsequent series of scans.

Experimental Procedure

In these experiments, you will utilize ionizing radiation to produce F -centers in a range of alkali halides. You will also investigate the effect of visible light on the stability of these color centers.

Choice of Crystals

Choose *five* crystals to irradiate from the suite supplied, employing some systematic scheme: for example, one could choose the chlorides of the different alkali ions, NaCl, KCl, RbCl and CsCl; or the fluoride, chloride, bromide and iodide of a single alkali, such as NaF, NaCl, NaBr, NaI. Include at least one crystal with the CsCl crystal structure in your set.

Irradiation-produced F -centers in Halide Crystals

Mount each crystal in an irradiation sample holder with two thin strips of black electrical tape and have the instructor insert these into the incident slit position in the X-ray diffractometer, nearest the X-ray source, where the X-ray flux is highest (with the X-rays OFF or at least the X-ray tube shutter closed!). Operate the rotating-anode X-ray tube at 60 kV and 30 mA (18-kW dissipation). Expose the crystals for 5 minutes (10 minutes if not deeply colored), then remove the holders from the X-ray source and **immediately store in the dark** by wrapping the holder in a small piece of aluminum foil. Crystals that are more hygroscopic (KBr, CsBr, CsI, RbBr, RbI) may have to be smeared before irradiation on both sides with a *very thin* film of vacuum grease to protect the surfaces from water condensation and attack, but try first without. Place the irradiated crystals in small envelopes and **label clearly**, so the crystals are not mixed up.

Using the Ocean Optics spectrophotometer, measure in turn the visible-light (~400-1000 nm) absorption spectrum of each of the crystals irradiated, noting the position of the most prominent absorption (F -band, usually) and any additional bands (*e.g.* likely candidates for the F_2 -band).

Plot the F -center absorption band position against the square of the lattice parameter a for the alkali halide crystals colored. Additionally note whether the F -band absorption for crystals with the CsCl structure falls on the trend line for the F -band absorption of NaCl-structure crystals, and make the appropriate correction if not. Calculate the effective diameter of the potential well in which the F -center electron is trapped as a fraction of the lattice parameter and, using the table of ionic radii supplied, see if the result appears reasonable in terms of assigning the observed absorption to an electron trapped in the potential of a halogen vacancy.

If there is time, expose either X -irradiated NaCl or X -irradiated KCl to bright light (room light or sun light or the spectrophotometer light) for about 15 minutes and re-measure the absorption to characterize any optical bleaching occurring. Briefly (5 minutes) irradiate the bleached crystal with a UV lamp (short wavelength setting) to see if the F -centers can be re-populated with electrons generated by UV irradiation and remeasure.

The F -center concentration induced can be estimated from the absorption coefficient measured if the penetration of the X -ray radiation is known. This will be an uncertain quantity because X -rays of different energy in the X -ray spectrum emerging from the X -ray generator penetrate different amounts and exhibit different efficiencies for F -center production. Assuming that the X -rays penetrate about 1 mm into the crystal, calculate an F -center density for the X -irradiation production. You may additionally assume the generation of X -rays is 1% efficient and that the X -rays are not absorbed appreciably in air. From the distance from the X -ray target to the irradiated sample, estimate the X -ray fluence (measured as total energy absorbed by the crystal per unit area) and calculate the absorbed energy required to produce one F -center.

References

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