

Color centers: An example of a particle trapped in a finite-potential well

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The wavelengths for color-center absorption can be determined from a simple quantum-mechanical model consisting of an electron trapped in a square finite-potential well. By varying the depth and width of this well we are able to adjust this model so that it predicts Ivey's relationship [$\lambda(\text{\AA}) = 73a^{1.80}$] between the F -center wavelength λ and the nearest-neighbor lattice spacing a . A more complicated model based on a spherical finite-potential well is also used to obtain Ivey's law. The depth and width of the well that fit this latter model to the F -center absorption data are then used to predict the wavelengths for the K , L , L_2 , and L_3 centers to -6% , 4.5% , 1.5% , and -1.0% respectively.

INTRODUCTION

Electrons trapped in ion vacancies of crystals like the alkali halides will absorb radiation in the visible spectrum and cause typically clear crystals to appear colored. The resulting effect is termed a color center, and its absorption characteristics can be determined from the energy eigenvalues of the trapped electron.

Consequently, color centers can be used in introductory courses, where quantum mechanics is first being introduced, as an example of a particle in a box. They can also be used in more advanced courses as an example of a finite-spherical well.

The simplest color center is the F center consisting of an electron trapped in a single negative-ion vacancy. The potential well of the F center can be modeled on several levels. Figure 1 shows a two-dimensional representation of an ionic-bond crystal with a negative-ion vacancy (labelled F). Since the four nearest ions are positive (all have donated their valence electrons to the halides), the vacancy looks like a minometal surrounded by a wall of positive charge. When an electron is introduced into this vacancy, it acts as a free electron trapped in a small volume defined by the surrounding negative ions. The simplest way to approximate the energy states of the electron in this region is to model the region by a cube with impenetrable walls (i.e., an infinite-potential well¹). In this model, we adjust the size of the cube so that the energy eigenvalues fit the experimental absorption data.

A more advanced approach uses a cubic potential well of finite depth. In this model there are two adjustable parameters, the width and depth of the well, which can be optimized to fit the model to the experimental data. A more sophisticated model of the F -center potential recognizes that in three dimensions the positive charges form an octahedron and not a cube. Since there is no analytical solution for the eigenvalues of an octahedral potential, we will approximate the potential as a spherical finite-potential well.

Experimentally, the absorption bands of color centers are measured by spectroscopic studies. The strongest absorption band for a particular halide is usually the F center. The *American Institute of Physics Handbook* contains a good collection of these data as compiled by Klick.² Ivey and Mollwo³ were the first to recognize that the peak position of the F -center absorption band is dependent on the lattice spacing of the halides. Using a least-squares analysis of

Klick's compiled data of the peak F -center wavelength λ versus the nearest-neighbor ion distance $a(\text{\AA})$ we find that

$$\lambda(\text{\AA}) = (732 \pm 43)a^{(1.80 \pm 0.05)}, \quad (1)$$

where the uncertainties represent the 67% confidence limits. The standard deviation of the experimental wavelengths from those predicted by this relationship was found to be $\pm 3\%$. Equation (1) agrees with Ivey's original relation⁴ within the uncertainty of the parameters, and thus, Eq. (1) will be called Ivey's law.

THEORETICAL MODELING OF THE POTENTIAL

Infinite-potential well

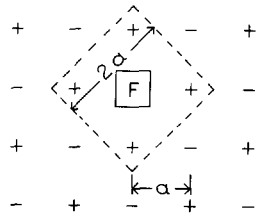
A number of simple models can be developed to explain the Ivey law. The simplest is to treat the electron as if it were trapped in a square-infinite-potential well. This is the most elementary problem in quantum mechanics and is often taught in introductory physics courses. According to this model the wavelength λ of the F center should correspond to the energy difference ΔE between the ground and the first excited states

$$\lambda = ch/\Delta E = ch(8ma^2/3\pi^2\hbar^2) \quad (2)$$

where c is the speed of light, m is the mass of the electron, h is Planck's constant, and $2a$ is the width of the well. For pedagogical purposes it should be noted that the same wavelength is obtained for a one-, two-, or three-dimensional solution. Thus, this model of the F center could be used in courses that have not advanced beyond the one-dimensional problem.

The model should now be used to determine what potential well size a best fits the F -center wavelength for each halide. Using Eq. (2) and the value of λ from Klick's data, a can be determined. On the average for each halide the value of a is found to be 16% larger than the nearest-neighbor lattice spacing a ($a = 1.16a$). Table I contains a list of the alkali halides with their F -center wavelength, their nearest-neighbor lattice spacing a , and the size of the infinite-square well (a) that fits this model to the experimental data. In the two-dimensional case (Fig. 1), we find that the potential with a size of a includes the four positive charges and omits the halides, thus agreeing with the original idea of the potential well defined by the negative ions.

Fig. 1. Two-dimensional representation of a square lattice with a nearest-neighbor spacing of a . A negative-ion vacancy occurs at F , which is the site of a possible F center. The dashed square indicates the first guess at the size of a potential well that would trap the F -center electron.



Finite-potential well

The infinite potential well represents a good method of model building, but even with adjusting a it still does not agree with the Ivey power dependence of λ on a . A more realistic approximation is to consider a potential well of finite depth. This potential provides us with two parameters to vary to fit the theory to Ivey's law. We will first vary the potential depth to get the correct power-law dependence. Then we will adjust the potential width to fit the model to the data.

The determination of the potential depth that fits the Ivey power dependence can be approached at two different levels. Introductory students can approach the problem with the aid of a computer. Given depth and width of the potential well they can use a computer to integrate Schroedinger's equation to obtain the energy eigenvalues by the shooting method.⁵ The F -center wavelength λ can be obtained in this way for a particular potential depth and width using $\lambda = ch/\Delta E$. Repeating the procedure while keeping the potential-depth constant and varying a from 2.01 Å for LiF to 3.66 Å for RbI the power dependence of λ on a can be determined. After doing this for several potentials the student can determine the potential that yields the power-law dependence of λ on a that agrees with Ivey's law. Since this can be an arduous procedure, it is advisable to give the student the correct potential of 47 eV and have him verify this value.

On the more advanced level the undergraduate should be able to study the power dependence on the potential depth by means of the analytical solutions to the finite-square well. One finds two transcendental equations whose solutions yield the energy eigenvalues for states of even and odd parity; namely,

TABLE I. F -center model-well sizes.

Alkali halide	a (Å) nearest-neighbor ion spacing	Klick's F -center wavelengths (Å)	a (Å) for square-infinite-well model	a (Å) for square-finite-well model	a (Å) for spherical-finite-well model
LiF	2.01	2500	2.38	2.07	2.46
NaF	2.31	3410	2.78	2.47	2.93
LiCl	2.57	3850	2.96	2.66	3.15
KF	2.67	4550	3.21	2.90	3.44
NaCl	2.81	4580	3.22	2.93	3.46
NaBr	2.98	5400	3.50	3.19	3.78
KCl	3.14	5560	3.56	3.26	3.86
NaI	3.23	5880	3.66	3.36	3.98
RbCl	3.27	6090	3.72	3.42	4.05
KBr	3.29	6250	3.77	3.47	4.11
RbBr	3.43	6940	3.97	3.66	4.34
KI	3.53	6890	3.96	3.66	4.34
RbI	3.66	7560	4.15	3.85	4.55

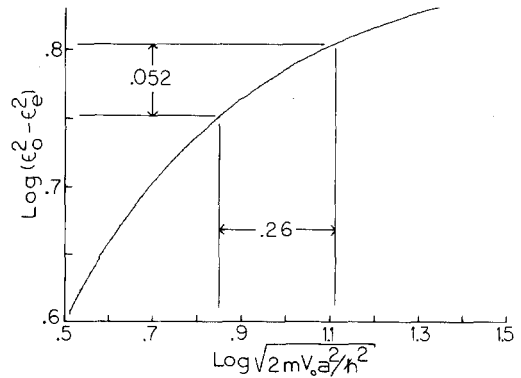


Fig. 2. A plot of $\log(\epsilon_0^2 - \epsilon_e^2)$ vs $\log(2mV_0a^2/\hbar^2)^{1/2}$ to determine the value of $\log(2mV_0a^2/\hbar^2)^{1/2}$, where the slope is 0.20. This value will determine the potential depth of the finite-square well that fits the Ivey power law for F -center data.

$$\epsilon \tan(\epsilon) = (2mV_0a^2/\hbar^2 - \epsilon^2)^{1/2} \quad (\text{even}), \quad (3)$$

$$\epsilon \cot(\epsilon) = -(2mV_0a^2/\hbar^2 - \epsilon^2)^{1/2} \quad (\text{odd}), \quad (4)$$

where

$$\epsilon = (2mEa^2/\hbar^2)^{1/2}. \quad (5)$$

V_0 is the potential depth, E is the energy of the state, and $2a$ is the full width of the well. Given values for V_0 and a the student can solve these transcendental equations numerically to obtain the energy eigenvalues. He can vary a and V_0 to find the correct power dependence for λ in the manner described previously.

A more systematic approach to the problem involves recognizing that we want to find the potential such that

$$\lambda \propto 1/\Delta E \propto a^{1.80} \text{ or } \Delta E \propto a^{-1.80}$$

where ΔE is the energy difference between the ground and first excited states. To determine ΔE Eq. (5) is rewritten in terms of E as

$$E = (\hbar^2/2m)(\epsilon^2/a^2), \quad (6)$$

where ϵ represents the roots of the transcendental equations. From Eq. (6), the change in energy is determined as

$$\Delta E = E_{\text{odd}} - E_{\text{even}} = (\hbar^2/2m)[(\epsilon_0^2 - \epsilon_e^2)/a^2], \quad (7)$$

where ϵ_0 is the root of the first excited state from Eq. (4) and ϵ_e is the root of the ground state from Eq. (3). (This relationship is true for the first excited state independent of the dimensionality of the problem.) Thus, from Eq. (7) we find we want a potential such that $(\epsilon_0^2 - \epsilon_e^2) \propto a^{0.20}$. The simplest way to determine this potential is to graph $\log(\epsilon_0^2 - \epsilon_e^2)$ vs $\log(2mV_0a^2/\hbar^2)^{1/2}$, as shown in Fig. 2. The correct value of $2mV_0a^2/\hbar^2$ can be obtained by finding the point on the graph where the slope is 0.20. Since we are trying to find one value of V_0 that works for all of the halides (with different values of a), we really don't want a single point where the slope is 0.20. We want a range of values

$$\Delta \log(\epsilon_0^2 - \epsilon_e^2) / \Delta \log[(2mV_0a^2/\hbar^2)^{1/2}] = 0.20,$$

where the change in the denominator is due to the change in the value of a for the different alkali halides (2.01–3.66 Å). Keeping V_0 constant the denominator $\Delta \log[(2mV_0a^2/\hbar^2)^{1/2}]$ becomes 0.26 when the above values of a are used. The appropriate Δy and Δx are indicated in Fig. 2. This evaluation yields a potential of $V_0 = 47$ eV.

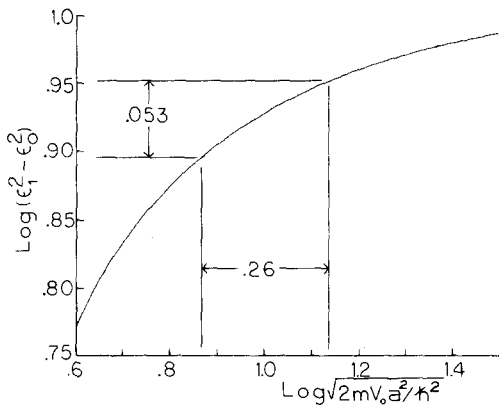


Fig. 3. A plot of $\log(\epsilon_1^2 - \epsilon_0^2)$ vs $\log(2mV_0 a^2 / \hbar^2)^{1/2}$ to help determine the potential depth of the finite-spherical well that fits the Ivey power law.

Now that the potential that gives the correct power dependence of λ on a is known we need to determine the width of the well that fits the theoretical wavelength to the F -center absorption peak. For each halide we will keep the $(\epsilon_0^2 - \epsilon_2^2)$ term as previously determined constant and then use Eq. (7) to determine the value of a that fits the model to the experimental data. Table I contains a list of the values of a compared to a for the halides. We find that the values of a for each halide are on the average 5% greater than a , the nearest-neighbor lattice spacing ($a = 1.05a$). This value of a is only 1% from the halfway point between the minimal well size that just surrounds positive ions at $a = a/\sqrt{2}$ and the maximum well size possible defined by the negative ions at $a = a\sqrt{2}$. In the determination of the potential depth V_0 the well size was assumed to be the nearest-neighbor distance a . Now that the value of the well size is known (a) we need to correct our value of the potential depth V_0 . Adjusting V_0 for the new spacing a we get $V'_0 = V_0 a^2 / a^2 = 42$ eV.

Finite-spherical well

A better model is a spherical finite-potential well. The previous potentials have been cubes in shape. While this is

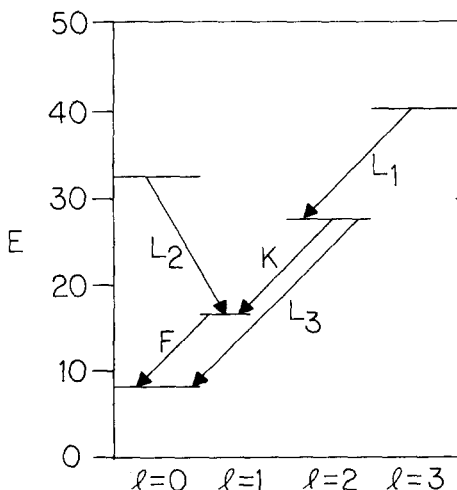


Fig. 4. An energy-level diagram of the energy states of a finite-spherical well with a lattice spacing similar to NaCl. The angular momentum associated with each state is labeled on the horizontal axis and the F , K , L_1 , L_2 , and L_3 transitions are labeled between the appropriate energy states.

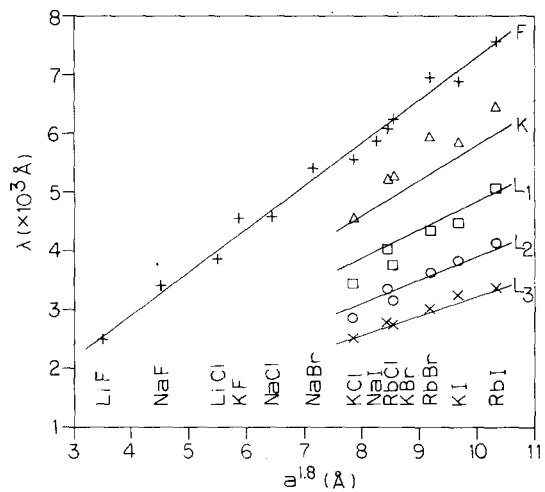


Fig. 5. A plot of the color center's wavelength vs the nearest-neighbor spacing a raised to the 1.80 power. The +, Δ , \square , \circ , \times indicate the F , K , L_1 , L_2 , and L_3 center data, respectively. The lines through the data are determined by the finite-spherical well theory for the F -center potential with the values of V_0 and a as determined from only the F -center data.

fine for the two-dimensional drawing of the crystal structure of the alkali halides, in three dimensions an octahedron represents the actual shape of the positive-ion structure.

This problem can be approached in the same manner as the finite-potential-square well. That approach is to study the solution to find the potential that best fits the Ivey power law and again use the results to determine the radius of the potential well. The ground-state energy level of the finite-spherical well can be found by solving the transcendental equation

$$\epsilon \cot(\epsilon) = -(2mV_0/\hbar^2 - \epsilon^2)^{1/2}, \quad l = 0, \quad (8)$$

where ϵ is as defined in Eq. (5), V_0 is the potential, and l is the angular-momentum eigenvalue. (Note that this is the same equation as the one that applies to the odd states for the finite well.) The first excited-energy state can be found by solving the transcendental equation⁶

$$[\epsilon \cot(\epsilon) - 1](2mV_0 a^2 / \hbar^2 - \epsilon^2) = \epsilon^2 [1 + (2mV_0 a^2 / \hbar^2 - \epsilon^2)^{1/2}], \quad l = 1. \quad (9)$$

Thus, the transition in this case is from a state having $l = 0$ to a state having $l = 1$.

In Fig. 3 we have drawn the graph of $\log(\epsilon_1^2 - \epsilon_0^2)$ vs $\log(2mV_0 a^2 / \hbar^2)^{1/2}$ for the spherical potential where ϵ_0 represents the smallest root of Eq. (8) and ϵ_1 represents the smallest root of Eq. (9). Upon completing an analysis similar to that performed on the cubic well we find the appropriate potential depth is 52 eV.

Keeping $(\epsilon_1^2 - \epsilon_0^2)$ constant, we can now use Eq. (7) to determine the well size a that will fit the model to F -center data for each halide. Table I contains a list of these values for the alkali halides. On comparing a to the nearest-neighbor lattice spacing a we find that a is an average of 24% larger than a ($a = 1.24a$).

This value gives a radius that includes the positive ions and is approximately halfway between the (1, 1, 1) plane going through the positive ions and the parallel plane going through the negative ions in the [1, 1, 1] direction. It should be pointed out that the values of V_0 have been determined using a , the nearest-neighbor spacing. If we adjust the potential for the new spacing a , we get $V'_0 = V_0 a^2 / a^2 = 34$ eV.

Extension of the model

Any model that is developed with one set of data should be verified by independent methods if possible. Since it has been shown experimentally² that four other absorption bands are related to the same potential as the F center; namely the K -, L_1 -, L_2 -, and L_3 -absorption bands, we will investigate whether the spherical-potential model can determine these resonances. We do this by studying the other energy states of the spherical potential. The relative-energy states for $l = 0, 1, 2,$ and 3 are drawn in Fig. 4 for NaCl. Using the values of the potential depth and width that were determined from the F -center data we have determined a close correlation between the K -, L_1 -, L_2 -, and L_3 -resonances and the higher energy transitions as labeled in Figure 4. In fact, the discrepancies between the predictions and the experimental values are -6% for K , 4.5% for L_1 , 1.5% for L_2 , and -1.0% for L_3 . (It should be noted that these transitions were determined entirely from changes in energy states and in fact the L_3 transition violates the $\Delta l = \pm 1$ selection rule for dipole radiation transitions on symmetric potentials.) Figure 5 is a plot of the experimentally determined values of the F , K , L_1 , L_2 , and L_3 bands. The line through the F -center data is that constructed from the spherical-potential model with $V_0 = 52$ eV and a increased by 24% . This line is indistinguishable from Ivey's law. The lines through the K , L_1 , L_2 and L_3 data points are again

those determined with the spherical potential as described above for the transitions indicated in Fig. 6. We have not gone into further detail here on the transcendental equations for obtaining the higher energy levels because they become very complicated.

CONCLUSION

We have presented a number of ways of studying a relatively simple phenomenon. On an elementary level, the color centers can be used as a good example of a particle in a box. On an advanced level, color centers can be used as a good example of spherical potentials and of model building where the model can be used to obtain information about the actual potential. In general, this model for the F center is very simple and agrees surprisingly well for a single model that is describing general trends of data.

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