THE JAHN–TELLER EFFECT:
A PEDAGOGICAL APPROACH

Y. Quéré

Laboratoire des Solides Irradiés *and* Département de Physique, Ecole polytechnique
Paris, France

Dedicated to Professor Dr. Julian Auleytner
on the occasion of his 70th birthday

Jahn–Teller effect and Stokes shift are presented in a simple, pedagogical approach adapted to students just starting their course of quantum mechanics. A simple experiment is suggested, which may illustrate and support semi-quantitatively this approach.

1. The Mollwo–Ivey law

Consider an alkali halide of NaCl structure and let a_0 be the lattice parameter of the elementary cube. Suppose that a vacancy has been created in the anion sublattice, for instance by X or γ irradiation. This vacancy tends to capture an electron, in order to restore locally the electrical neutrality. The association of this vacancy and of this electron is the well-known F-centre.

The shape of the vacancy is, in first approximation, an empty cube of edge a_0. If this is taken as a cubic well of infinite potential barrier, the possible states for the electron inside the cube are immediately written as

$$\psi_1 = \left(\frac{2}{a_0}\right)^{3/2} \sin\frac{\pi}{a_0}x \sin\frac{\pi}{a_0}y \sin\frac{\pi}{a_0}z, \qquad E_1 = \frac{\hbar^2}{2m}\frac{3\pi^2}{a_0^2}, \qquad (1)$$

$$\left.\begin{array}{l} \psi_{2x} = \left(\frac{2}{a_0}\right)^{3/2} \sin\frac{2\pi}{a_0}x \sin\frac{\pi}{a_0}y \sin\frac{\pi}{a_0}z, \\[2mm] \psi_{2y} \\[2mm] \psi_{2z} \end{array}\right\} \qquad E_2 = \frac{\hbar^2}{2m}\frac{6\pi^2}{a_0^2}, \qquad (2)$$

$\cdots$

The ψ's are equal to 0 outside the cube; m = electron mass and $\hbar = h/2\pi$. A student will, here, show easily that these states are not eigenstates of the angular momentum, due to the non-centrality of the cubic potential.

A transition of type $\psi_1 \rightarrow \psi_2$ absorbs an energy

$$\Delta E_{\text{abs}} = E_2 - E_1 = \frac{\hbar^2}{2m} 3\pi^2 a_0^{-2}, \tag{3}$$

where we recognize the celebrated Mollwo–Ivey law which states that the energy of photon absorption lines in irradiated alkali halides of crystal parameter a_0 has approximately an a_0^{-2} dependence. In spite of the roughness of the previous
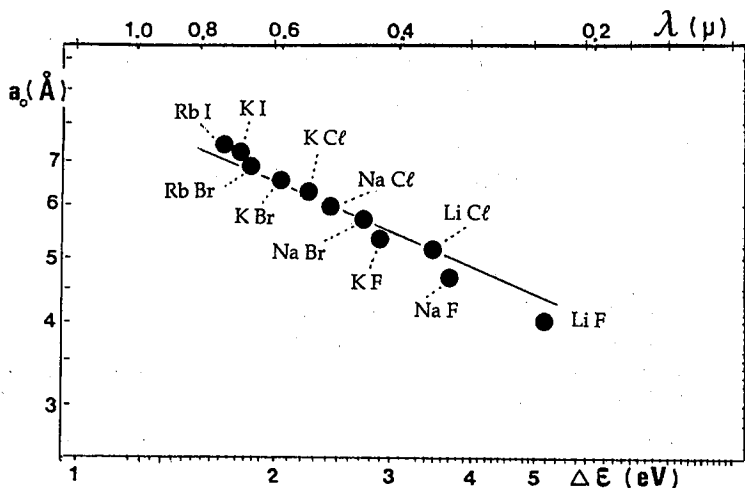

Fig. 1. Energy ΔE (in eV) — or wavelength λ (in μm) — of the main absorption line in a number of alkali halides of lattice parameter a_0. Circles: experimental values. Straight line: function $(\hbar^2/2m)3\pi^2(\alpha a_0)^{-2}$ (see (3) and (4)); $\alpha = 1.08$.

arguments, the experiments are reasonably well reproduced by (3) (see Fig. 1) if the constant part of (3) is divided by $\alpha^2 = 1.16$ (97 eV Å^2 instead of 113 in (3)). This numerical factor just represents the fact that the electron is situated in an "effective" cubic well of edge $a = \alpha a_0$ larger by 8% than the lattice parameter a_0, a normal tendency if one considers the presence of six positive ions on the border of the well. The straight line in Fig. 1 takes this numerical correction into account. Later on, we put

$$\frac{\hbar^2}{2m} \frac{\pi^2}{a^2} = K \quad \text{and} \quad a = \alpha a_0. \tag{4}$$

2. The Jahn–Teller effect

If the quantum state of a molecule is degenerate, there exists a distortion of the molecule which, lowering the symmetry, removes the degeneracy and stabilizes the molecule [1]. This is called a "Jahn–Teller distortion", an idea which will be now applied to the previous simple cubic F-centre.

Consider the simple distortion which transforms the previous effective cube (edge a) into a tetragonal well (edges b along z and c along x and y) at constant volume $a^3 = bc^2$, and let $\eta = b/c$ be the "distortion parameter". State ψ_{2z} is "distorted" into state ψ'_{2z} with

$$\psi'_{2z} = \frac{2}{c}\left(\frac{2}{b}\right)^{1/2} \sin\frac{\pi}{c}x \sin\frac{\pi}{c}y \sin\frac{2\pi}{b}z,$$

$$E'_{2z} = \frac{\hbar^2\pi^2}{2m}\left(\frac{2}{c^2} + \frac{4}{b^2}\right) = K(2\eta^{2/3} + 4\eta^{-4/3}). \tag{5}$$

In the same way, we calculate

$$E'_{2x} = E'_{2y} = K(5\eta^{2/3} + \eta^{-4/3}). \tag{6}$$

It is clear that both E'_{2z} and E'_{2x} are different from E_2 as soon as η is different from one, that is as soon as a distortion is created: the distortion removes the threefold degeneracy of the ψ_2 excited states. One finds immediately that E'_{2z} has a minimum for the value $\eta = 2$ whereas E'_{2x} has a minimum for $\eta = \sqrt{2/5} = 0.63$ and that these minima are respectively $4.76K$ and $5.52K$.
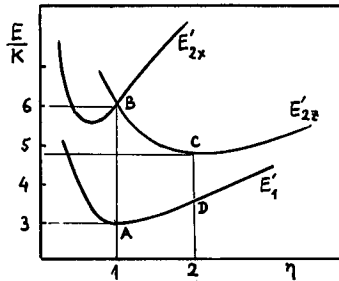

Fig. 2. Variations of some energy levels of the F-centre expressed in units of K (see (4)), versus distortion parameter η, from (5), (6) and (7).

Both are smaller than $E_2 = 6K$ (see (2) and (4)), the first one being a minimum minimorum (Fig. 2). We conclude that the system, in its excited state, is stabilized when distorted by $\eta = 2$, i.e. for an elongated shape of the F-centre ($\eta > 1$).

3. Stokes shift

We have now to understand the following experimental fact. After a lifetime of the order of 10 μs, the excited centre, in its Jahn–Teller distorted state, emits a luminescence photon. The experimental observation of the emission lines shows that these lines, as compared to the absorption lines of the same crystal, are systematically shifted towards smaller energies: this is the Stokes shift, an example of which is shown in Fig. 3.

Considering Franck–Condon principle according to which the excitation and deexcitation times are negligible as compared to the times of local atomic deformation, which are themselves negligible as compared to lifetimes of excited states
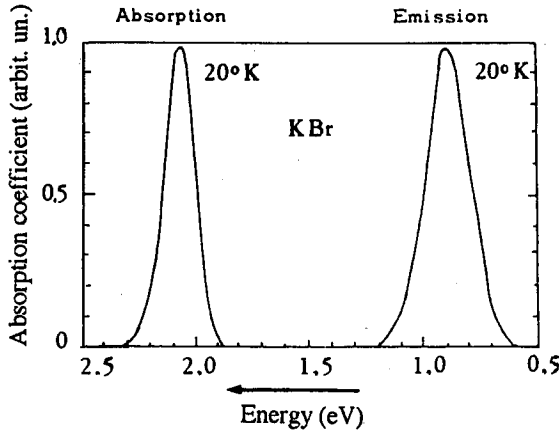
Fig. 3.   Absorption and emission spectra of the F-centre in KBr measured at low temperature. Maxima of both lines are situated at 2.06 and 0.92 eV [2].

($\approx 10~\mu$s), we must consider the deexcitation from the distorted state ψ'_{2z} to the distorted state ψ'_1. The latter is expressed by

$$\psi'_1 = \frac{2}{c}\left(\frac{2}{b}\right)^{1/2}\sin\frac{\pi}{c}x\sin\frac{\pi}{c}y\sin\frac{\pi}{b}z$$

with energy

$$E'_1 = K(2\eta^{2/3} + \eta^{-4/3}). \qquad (7)$$

The variation of E'_1 versus η is shown in Fig. 2. A minimum appears for $\eta = 1$ i.e. for the non-distorted centre, whereas the energy has the value $3.57K$ for the elongated shape $\eta = 2$. The deexcitation of the elongated centre then emits a photon of energy

$$\Delta E_{\text{em}} = E'_{2z}(2) - E'_1(2) = (4.76 - 3.57)K = 1.19K. \qquad (8)$$

This is smaller than the absorption energy $3K$ (see (3) where a_0 has been replaced by a) and we have $\Delta E_{\text{em}}/\Delta E_{\text{abs}} = 0.40$ which compares fairly well with the experimental ratio ≈ 0.44 measured in KBr in Fig. 3.

The absorption–emission cycle can then be traced in Fig. 2: AB corresponds to the absorption of a photon in the cubic F-centre; BC to the cubic $\rightarrow$ tetragonal deformation of the centre in its first excited state; CD to the emission of a deexcitation photon in the elongated state; DA to the return of the centre to its stable cubic shape. Both BC and DA are accompanied by phonon emission.

4. A simple pedagogical experiment

A direct demonstration of the absorption of F-centres can then be made. Having shown numerically, from (8), that the emission lines are situated in the infrared domain, the students will understand that the colour of an irradiated alkali halide is a signature of the absorption only.

One then irradiates with X- or γ-rays some crystals of a few alkali halides, like NaCl, KCl, and KI. They become respectively yellow, purple and green. It is suggested to ask the students who have made the previous simple evaluations to distinguish, from the colour, these crystals from each other. They will just have to remember that the colour seen is the complementary colour of that absorbed. The yellow crystals thus absorb in the violet, which means that the absorption lies in the band 2.65–3.1 eV. From Fig. 1 it will be deduced that these are NaCl crystals. In the same way, the complementary to green is red (and purple is complementary to yellow), with energy band 1.65–2.0 eV (respectively 2.1–2.3 eV). From Fig. 1 again, the green crystals will be called KI (respectively KCl).

The last experiment will then consist in heating slightly the crystals with the flame of a match and showing (possibly with a back projector) the disappearance of the colour, an indication of the vacancy diffusion to permanent sinks. The finally recovered transparency of the crystals will give a clear (!) evidence of the non-intrinsic character of the observed colours, in contrast to such solids as sulphur where the colour is due to an intrinsic property of the band structure.

References

[1] H.A. Jahn, E. Teller, *Proc. R. Soc. Lond. A* **161**, 220 (1937).

[2] W. Gebbart, A. Kuhnert, *Phys. Status Solidi* **14**, 157 (1966).