

If, as we suggest, creep is more likely when there are Néel walls in the film, then creep may be expected in those field configurations which result in the formation of Néel walls. Here we may well have the explanation of Middelhoeck's experimental results which show that creep does indeed seem in some way related to wall transitions from either Bloch, or cross-tie, to Néel.

Although the mechanism we put forward is concerned primarily with Néel walls, there is nevertheless the possibility that a similar, though smaller, structural change may occur involving only Bloch or cross-tie walls. This aspect remains to be investigated in later work.

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¹ Middelhoeck, S., "Domain Walls in Thin Ni-Fe Films", *I.B.M. Res. Rep.* RC 846 (December 1962).

Primary and Subsidiary Condon Loci of Molecular Spectra

THE Franck-Condon principle¹ predicts that the vibrational quantum numbers v' , v'' of the strongest bands of a molecular spectrum lie on a family of open double-lobed quasi-parabolic curves in the $v'v''$ plane which are often roughly coaxial about $v' = v''$. The curves are called the primary (outermost) and subsidiary (inner) Condon loci. The loci are indicated on a number of recently published Franck-Condon factor arrays²⁻⁴. The smaller the difference Δr_e between equilibrium internuclear separations r'_e and r''_e of the molecular potentials involved, the narrower are the loci and the closer is the apex of the primary locus to (0, 0). The greater Δr_e , the more open the loci, and the further the apex of the primary locus is from (0, 0) down the diagonal $v' = v''$. The apices of the subsidiary loci are often spaced roughly two quantum numbers apart down the diagonal axis.

Apart from brief semi-classical discussions of the shape of the primary locus^{5,6}, little comment has been made on their geometry from a quantum point of view. The geometry of the primary and subsidiary loci, which is therefore discussed here, has obvious applications to identifications of molecular spectra in addition to being of general spectroscopic interest.

Intense bands have large Franck-Condon factors $q_{v'v''} = |\int \psi_{v'} \psi_{v''} dr|^2$ for which the non-cancelling overlap between vibrational wave functions ψ_v is large. Large overlap usually occurs when an antinode of one wave function and an antinode of the other wave function lie in the same region of r . The primary Condon locus passes through those v' , v'' values for which the largest contribution to $q_{v'v''}$ occurs by strong overlap between pairs of terminal (outer) antinodes. Similarly the subsidiary loci pass through v' , v'' values for which the largest contribution to $q_{v'v''}$ occurs by overlap between terminal and subsidiary antinodes.

The Franck-Condon principle, which in classical terms calls for equality of oscillator turning points⁶, can thus be recast in quantum terms by calling for equality between the positions of an appropriate pair of antinodes, one for each of the levels involved.

Pairs of antinodes of order p are equally spaced about r_e for potentials which are symmetrical about r_e . There are $w+1$ such pairs of antinodes for even ($v=2w$) and for odd ($v=2w+1$) vibrational levels. The p 'th antinodes of the v 'th level of a symmetrical potential thus lie at $r_{v1}(p)$ and $r_{v2}(p)$ where:

$$r_{v1}(p) = r_e - F_v(p) \quad (1a)$$

$$r_{v2}(p) = r_e + F_v(p) \quad (1b)$$

$F_v(p)$ is the separation between the p 'th antinode and r_e . It depends on the specific form of the potential. For a simple harmonic potential it is possible to show that:

$$F_v(p) = (k\omega)^{-1/2} \left\{ \frac{v - b_p}{a_p} \right\}^{1/n_p} \quad (2)$$

where $1 < a_p < 3.5$; $b_p = 2(p-1)$, $1 < n_p < 2$, $0 < p < 10$, $k = 4\pi^2 \mu c/h$ and ω is the oscillator frequency in cm^{-1} .

As the Franck-Condon principle calls for equality of antinode positions, the primary locus is:

$$r_{v'1,1}(1) = r_{v''1,1}(1) \quad (3a)$$

and the p 'th subsidiary locus lies in the region where:

$$r_{v'1,2}(1,p) = r_{v''1,2}(p,1) \quad (3b)$$

For a simple harmonic potential, equation (3a) may be rewritten, using equations (1a), (1b) and (2), as:

$$\pm k^{1/2} a_1^{1/n_1} \Delta r_e = \pm \frac{(v' - b_1)^{1/n_1}}{\omega^{1/2}} \pm \frac{(v'' - b_1)^{1/n_1}}{\omega^{1/2}} \quad (4)$$

where Δr_e is the magnitude of $r' - r''_e$. Equation (4) represents the primary locus in the v' , v'' plane.

The choice of signs implied in equation (4) allows it to take the following physically meaningful forms:

$$\Delta r_e = V_1' a_1 + V_1'' a_1 \quad (5a)$$

$$\Delta r_e = V_1' a_1 - V_1'' a_1 \quad (5b)$$

$$\Delta r_e = V_1'' a_1 - V_1' a_1 \quad (5c)$$

where $a_1 = 1/n_1$ and $V_1 = (k\omega)^{-1/2} a_1 (v - b_1)/a_1$. The gross regional overlap between the two potentials involved determines where each of these equations is used to represent segments of the primary Condon locus as follows.

When Δr_e is sufficiently large that only one limb of one potential curve (for example, $r < r'_e$ or $r > r'_e$) lies in the same range of r as the other limb of the other potential curve ($r > r''_e$ or $r < r''_e$) equation 5a represents the primary Condon locus. It is a broad curve, well separated from (0, 0).

On the other hand, when Δr_e is small so that there is complete overlap between all of each potential, three segments (a, b, c) have to be treated separately. They are:

- (i) If $r'_e > r''_e$; (a) $r < r''_e$, (b) $r''_e < r < r'_e$, (c) $r > r'_e$
- (ii) If $r''_e > r'_e$; (a) $r < r'_e$, (b) $r'_e < r < r''_e$, (c) $r > r''_e$

Equation (5a) represents segments (ib) and (iib). Equation (5b) represents segments (ia) and (iic). Equation (5c) represents segments (ic) and (iia). In each of these cases, equation (5b) represents the apex of the locus and equations (5a) and (5c) represent the limbs.

Equations 5a, 5b, 5c have been plotted for a number of band systems and have been found to represent the primary locus quite well for moderate values of quantum numbers ($v \sim 10$) in spite of the obvious limitations of the potential used. Similar treatment of equation 3b has led to adequate representation of the subsidiary loci.

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