

Superlattice and quantum-size effect (QSE) in the intercalated crystals

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A three-dimensional QSE was observed in bulk samples for the first time. It was investigated in layered PbI_2 crystals intercalated by organic molecules.

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Since the time it was predicted,⁽¹⁾ the quantum-size effect was observed many times in thin films or colloidal particles when the linear dimensions of the potential well were defined by the dimension of the sample. In this paper, we report the observation of the quantum-size effect in objects whose linear macroscopic dimensions are unlimited and the effect is determined by the characteristic equilibrium spacing of the given crystal structure—the intercalated layered crystal.

Koshkin *et al.*⁽²⁾ showed that the different, donor-type organic molecules introduced into the PbI_2 crystal with a layered lattice are ordered in the van der Waals gaps of the matrix crystal, so that a superlattice with a large spacing a , which is a multiple of the spacing a_0 of the original hexagonal PbI_2 lattice, is formed. The introduction of intercalating molecules increases the spacing between the layers D . The values of a and D for the different intercalating molecules in the PbI_2 matrix are given in Table I.

The quantum-size effect can be observed in the spectra of the diffuse reflection coefficient $R_d(\epsilon)$ (ϵ is the quantum energy) of the intercalating crystal power and of the original PbI_2 . It seems that after intercalation the edge of the fundamental absorption band undergoes an appreciable shortwave shift ΔE , which is different for different intercalating molecules. The values of ΔE are given in Table I.

The location of the edge of the absorption band was determined from the half-decay of $R_d(\epsilon)$.

We can assume that since the intercalating molecules produce a potential relief, the quasi two-dimensional potential wells with linear dimensions a appear in the PbI_2 layer.

For a square well with infinitely high walls the energy of the particle, which is governed by the isotropic, two-dimensional dispersion law, is

$$E_{n_x, n_y} = \frac{\hbar^2}{8m^*} \frac{1}{a^2} (n_x^2 + n_y^2), \quad (1)$$

where h is the Planck constant, m^* is the effective mass of the particle, and $n_x, n_y = 1, 2, 3, \dots$ are integers.

The energy of the lowest resolved state with $n_x = n_y = 1$ is higher than that of the well bottom by the amount

TABLE I. Structural and Optical Parameters of the Intercalated Crystals.

Substance	a , Å	c , Å	ΔE , eV
PbI ₂	$a_0 = 4.59$	6.86	—
PbI ₂ -quinoline	$4a_0 = 18.4$	29.9	0.43 + 0.03
PbI ₂ -aniline	$4a_0 = 18.4$	20.5	0.40 + 0.01
PbI ₂ -nonylamine	$5a_0 = 23.0$	62.0	0.30 + 0.03
PbI ₂ -decylamine	$6a_0 = 27.6$	73.4	0.25 + 0.02
PbI ₂ -dimethyl cetylamine	$7a_0 = 32.2$	61.0	0.22 + 0.03
PbI ₂ -piperidine	$a_0 = 4.59$	14.1	0.15 + 0.02

a_0 is the lattice constant of PbI₂, c is the parameter of the hexagonal cell in the z direction, which in the intercalated compounds corresponds to an increase of the interlayer distance D . The structural parameters a_0 , a , and c are given in Ref. 2.

$$E_{1,1} = \frac{2}{8} \frac{\hbar^2}{m^*} \frac{1}{a^2} \quad (2)$$

An increase in the energy of the ground state shifts the edge of the absorption band $\Delta E = E_{1,1}$. It follows from Eq. (2) that, for a given matrix crystal with a constant m^* , ΔE is a linear function of $1/a^2$.

The indicated linear correlation between ΔE and $1/a^2$ can be experimentally observed (see Fig. 1), which indicates that the quantum-size effect is present in the plane of the PbI₂ layer and that the potential wall is higher than the energy of the lowest state.

The equation for the straight line in Fig. 1 is

$$\Delta E \text{ (eV)} = 100 \frac{1}{a^2} + 0.13, \quad (3)$$

where a is in angstroms.

Although the observation of quantum-size effects in the quasi two-dimensional PbI₂ layers as a result of ordering of the intercalating molecule is consistent with the concept of minizones in such superlattices,^[3] the function of the minizones of the valence and conduction bands in optical absorption requires further explanation.

We note that the straight line in Fig. 1 is not extrapolated to zero. We are inclined to attribute the term in Eq. (3), which appears on the Y axis due to this cut-off, to size quantization in the direction of the z axis perpendicular to the PbI₂ layers. In this case the width of the well is the layer thickness d of the three-layer packet I-Pb-I and the energy of the particle is given by

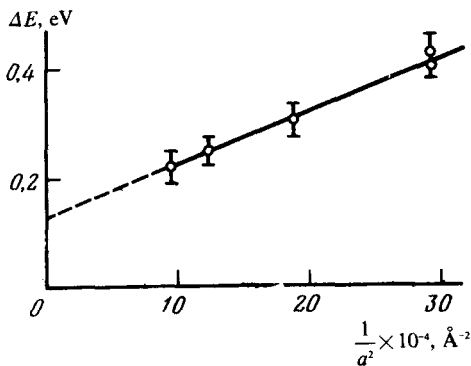


FIG. 1.

$$E_{n_x, n_y, n_z} = \frac{\hbar^2}{8m^*} \left[\frac{n_x^2 + n_y^2}{a^2} \right] + \frac{\hbar^2}{8m_z^*} \frac{n_z^2}{d^2}. \quad (4)$$

For the lowest resolved state

$$E_{1,1,1} = \frac{\hbar^2}{8m^*} \frac{2}{a^2} + \frac{\hbar^2}{8m_z^*} \frac{1}{d^2}. \quad (5)$$

If the last terms in Eq. (5) and in the empirical equation (3) are identified, then we can conclude that this energy shift, which is constant for every intercalating molecule in the given crystal matrix, is the energy of the lowest state in the quasi one-dimensional block with a linear dimension equal to the thickness of the layer of the original matrix (z shift).

An additional confirmation of this model is the result obtained in the piperidine intercalation when the superstructure is not detected.⁽²⁾ In this case the superlattice constant and hence the linear dimensions of the two-dimensional well are infinite. Therefore, the first term in Eq. (5) should vanish and ΔE for piperidine intercalation should coincide with the second term in Eqs. (3) and (5). We observed this experimentally. For piperidine $\Delta E = 0.15$ eV (see Table I), which exactly coincides with the "cut-off" in the given diagram (0.13 ± 0.02 eV).⁽¹⁾

We can draw two conclusions from this. First, the z shift, which occurs as a result of intercalation, indicates that prior to intercalation a nonzero overlap of the wave functions occurs between the layers (via the van der Waals gap).

The extent of this overlap is such that the delocalization of electrons corresponding to it decreases their energy by at least 0.13 eV compared to the isolated layer. The indicated effect undoubtedly occurs in all layered structures. Second, the fact that the z shift of the intercalating crystals does not depend on D (see Table I) indicates that the layer overlapping of the wave functions decreases rather sharply with the distance, so that none of the intercalating structures apparently has such overlap.

Thus, the results show that the intercalated layered crystals have a pronounced,

three-dimensional quantum-size effect, which is an intrinsic property of such crystal structures in contrast to all other cases in which the quantum-size effect is produced artificially by specially selecting the samples according to size.

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¹We have not made a very large error by examining a three-dimensional square well rather than a prismatic well with a hexagon at the base. In fact, the lowest state in the cubic well with a linear dimension a is

$$\frac{3}{8} \frac{\hbar^2}{m^*} \frac{1}{a^2}$$

The lowest state in a spherical well with a diameter a and infinitely high wells is

$$\frac{4}{8} \frac{\hbar^2}{m^*} \frac{1}{a^2} \quad (4)$$

The corresponding values for the described polyhedrons with a larger number of vertices than that of a cube are situated between these values. Note, however, that the potential at the boundary of the well in the investigated case is probably not a rectangle. Although the spectrum does not depend on the depth of the well if it is sufficiently deep, the shape of the potential may affect significantly the coefficient at $1/a^2$. Therefore, we shall not determine the value of m^* according to the dependences (3) and (5).

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