Superlattice, miniband spectrum, and phase transition in the intercalation semiconductor PbI_2–quinoline

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(Submitted 28 January 1986)
Zh. Eksp. Teor. Fiz. **91**, 1702–1707 (November 1986)

A structural phase transition in PbI_2–quinoline crystals at $T_c = 190$ K is observed by low-temperature x-ray analysis. The temperature dependence of the luminescence and excitation spectra reveals a phase transition in which the superlattice period doubles from $a = 4a_0$ ($T > T_c$) to $a = 8a_0$ ($T < T_c$). The parameters of the electron miniband spectrum for PbI_2–quinoline are estimated.

Intercalation compounds result when, e.g., organic molecules are incorporated into van der Waals interstices in multilayer inorganic matrices. Most of the research interest on phase transitions in layered crystals and their intercalation compounds has centered on the dichalcogenides of the transition metals, which exhibit metallic conduction.[1] However, there is an extensive class of semiconductor and dielectric layered crystals and intercalation compounds whose phase transitions are virtually unstudied (see the review in Ref. 2).

Intercalation semiconductors have several distinctive properties. For example, it was shown in Ref. 3 that because the long-range dipole-dipole interaction between the intercalated molecules is not screened by free electrons, the concentration and temperature dependences of the molecules are transferred to the matrix layers. This effect is in many respects analogous to the concentration-induced change in the effective charge of atoms absorbed on submonatomic layers.[4] The phase diagram was found in Ref. 3, where it was predicted that semiconductor intercalation compounds may contain several phases which have unequal superlattice periods and hence distinct two-dimensional electron miniband spectra. If such materials could be found, it would be possible to adjust the miniband spectrum by changing the temperature and the concentration of the intercalated molecules, and this forms the subject of the present paper.

X-ray data and diffuse reflection spectra were analyzed in Refs. 5 and 6, respectively, and it was shown that the intercalation semiconductor PbI_2–quinoline has a superlattice with period $a = 4a_0$, where a_0 is the PbI_2 lattice parameter in the plane of the layers. The superlattice consists of ordered quinoline molecules that are incorporated in the van der Waals interstices between the layers of the PbI_2 crystal. We carried out an x-ray structure analysis of PbI_2–quinoline and studied its luminescence and excitation spectra in order to verify experimentally that phase transitions that alter the superlattice period can occur in intercalation compounds.

1. Owing to difficulties in obtaining high-quality single crystals, the structure of the overwhelming majority of intercalation compounds (including PbI_2–quinoline) has not yet been established with certainty. We therefore employed powder x-ray analysis using a DRON-3 diffractometer in our work. A URNT-180 low-temperature attachment was used to cool the powder and maintain it at a constant temperature, which was measured precisely by stamping an independent thermocouple into the specimen.

The specimens contained both heavy (Pb,I) and light atoms (C,N,H). Because the depth of the semiabsorbing layer for the light atoms was considerably greater than for the heavy atoms,[7] the latter determined the form of the x-ray diffraction patterns almost completely.

Throughout the 100–300 K temperature range considered the diffraction patterns for the finely ground powder were identical, except for a small change in the angular position of the lines; the line widths and relative intensities were virtually identical. By using a coarser powder (grain diameter ~0.1mm) obtained as described in Ref. 8, we were able to enhance the intensity of individual lines corresponding to higher diffraction angles and thereby perform measurements out to $2\vartheta \sim 120°$. This permitted us to measure changes in the interplane distance with a relative error of better than 2 parts in 10^4.

Figure 1 shows the temperature dependence of the relative change in one of the interplane distances for a PbI_2 crystal and for PbI_2–quinoline. Although the curve for PbI_2 is linear, the dependence for PbI_2–quinoline has a kink which indicates the presence of a second-order phase transition (or a first-order phase transition with $\Delta d/d \lesssim 2 \cdot 10^{-4}$) at $T_c = 190$ K. Since no changes were discernible in the powder x-ray diffraction patterns for $T \approx T_c$, this indicates that the structural changes primarily affected the outlying atoms

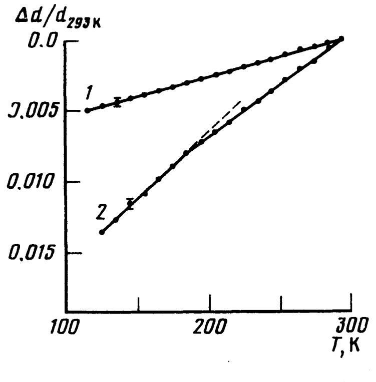

FIG. 1. Temperature dependence of the relative change in the interplane distance corresponding to a large-angle x-ray diffraction line for PbI_2–quinoline and pure PbI_2 (top line).

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and influenced the heavy atoms in the matrix only weakly (by altering the linear expansion coefficient). As was noted above, it is the latter that give the dominant contribution to the x-ray diffraction pattern.

2. Although the diffraction patterns reveal a phase transition and give the transition temperature, they do not determine the nature of the transition. To ascertain if the superlattice period changes as predicted in Ref. 3, it is natural to consider the electron spectra, since changes in the superlattice period are accompanied by corresponding changes in the miniband spectrum for the electrons.[9] Since we are interested here only in the qualitative behavior, we consider the simplest possible model of a two-dimensional electron gas in a periodic field with principal period a_0 measured along a fixed direction. We assume that a superlattice with period $a = na_0$ extending along the same direction is present (here n is an integer). No closed expressions are available for the dispersion law for the general case when the lattice period increases n-fold (see Ref. 9 and the literature cited there), nor can the absorption coefficient be calculated in closed form. We therefore use the close coupling approximation and write the electron dispersion laws for the conduction (c) and valence (v) subbands in the form[1)]

$$\varepsilon_v{}^i=\varepsilon_v{}^{0i}-p_y{}^2/2m_v{}^i-(-1)^i\Delta_v{}^i\cos p_x a, \tag{1}$$

where $i = 1,2,...$ labels the subbands above (c) and below (v) the forbidden band, $\Delta^i_{c(v)}$ is the halfwidth of the ith conduction (valence) subband, and $\varepsilon^{0i}_{c(v)}$ is the position of the center of the ith conduction or valence subband. The gap between subbands i and $i+1$ in the conduction band, for example, is equal to $\delta_i = \varepsilon^{0c}_{i+1} - \varepsilon^{0c}_i - (\Delta^i_c + \Delta^{i+1}_c)$. In this case the absorption coefficient for light at frequency ω is equal to [we take $\hbar = 1$ in Eq. (1) and below]

$$\alpha(\omega)=\sum \alpha_{ij}(\omega), \tag{2}$$

where $\alpha_{ij}(\omega)$ is the contribution to α from electron transitions from valence subband j into conduction subband i. An expression for $\alpha_{aj}(\omega)$ that includes only direct transitions is readily derivable from Ref. 11, for example:

$$\begin{aligned}
&\alpha_{ij}(\omega)=0, \quad \omega^{ij}<\Delta^{ij},\\
&\alpha_{ij}(\omega)=\frac{1}{(2\omega\Delta^{ij})^{1/2}}K\left(\left(\frac{\Delta^{ij}+\omega^{ij}}{2\Delta^{ij}}\right)^{1/2}\right), \quad |\omega^{ij}|\leqslant\Delta^{ij}, \qquad (3)\\
&\alpha_{ij}(\omega)=\frac{1}{(\omega(\Delta^{ij}+\omega^{ij}))^{1/2}}K\left(\left(\frac{2\Delta^{ij}}{\Delta^{ij}+\omega^{ij}}\right)^{1/2}\right), \quad \omega^{ij}>\Delta^{ij},
\end{aligned}$$

where

$$\omega^{ij}=\omega-\varepsilon_g{}^{ij}, \quad \varepsilon_g{}^{ij}=\varepsilon_c{}^{0i}-\varepsilon_v{}^{0i}, \quad \Delta^{ij}=|(-1)^i\Delta_c{}^i+(-1)^j\Delta_v{}^j|,$$

and $K(x)$ is the complete elliptic integral. It is clear that the absorption spectrum, which consists of n^2 terms, acquires additional poles as the multiplicity n of the superlattice increases. For example, for a phase transition from $n = 1$ to $n = 2$, the electron spectrum should acquire, in addition to absorption peaks that correspond to the $v^1 \to c^1$, $v^2 \to c^2$ transitions and are already present in the $n = 1$ phase, an additional absorption due to $v^1 \to c^2$, $v^2 \to c^1$ transitions between the subbands. According to the momentum selection rules, this absorption is absent in the $n = 1$ phase. Figure 2 shows some characteristic absorption spectra calculated using (2) for $n = 1,2,3,4,8$. The groups of maxima corresponding to the Van Hove peaks in the state densities for the subbands are clearly visible. Of course, a detailed comparison of theory with experiment is not possible owing to the crudeness of our model and the limited resolution of the experimental spectra. However, the theoretical curves $\alpha(\omega)$ show that the changes in the spectrum during the phase transition are discontinuous; this is because they are caused by the change in the symmetry. The form of the absorption spectrum therefore differs markedly for phases with different n. For a fixed n, the absorption spectrum is quite insensitive to the width Δ of the subbands and the gaps δ between them; changes in Δ and δ merely shift the peaks without altering the overall spectrum. The discontinuous change in the form of the spectrum during the phase transition can be recorded experimentally.

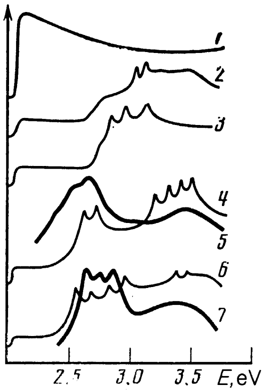

FIG. 2. Theoretical absorption spectra for a crystal with a superlattice for several multiplicities and orderings: 1) $n = 1$; 2) 2; 3) 3; 4) 4; 6) 8; luminescence excitation spectra for PbI_2–quinoline at $T = 180$ (5) and 200 K (7).

3. Since it is difficult to record the frequency dependence $\alpha(\omega)$ experimentally for fine powders, we analyzed the luminescence and excitation spectra for the Pb_2I–quinoline intercalation crystals. These spectra are closely correlated with the absorption spectra. The luminescence spectra were recorded using an SDL-1 spectrophotometer for temperatures from 80 to 300 K. The luminescence was excited by a DKSSh-120 xenon lamp and MDR-2 monochromator. Luminescence spectra for several temperatures are shown in Fig. 3. The luminescence excitation spectra were analyzed for several wavelengths within the luminescence band. They were all found to have the form shown in Fig. 2 for several temperatures. Both the luminescence and the luminescence excitation spectra reflect the properties of the entire PbI_2–quinoline coordination complex and not just the properties of the quinoline, whose luminescence and absorption spectra lie at substantially shorter wavelengths.[12] The excitation spectra above and below the critical point T_c are seen to differ radically. The band at 2.6–2.8 eV in the luminescence excitation spectrum disappears as T passes through T_c; according to the above calculation, this corresponds to a tran-

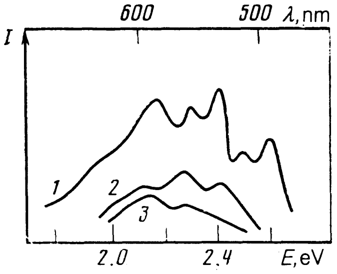

FIG. 3. Luminescence spectra for PbO_2–quinoline at 4.2 (1), 180 (2), and 200 K (3).

sition from a phase with larger n ($T < T_c$) to a phase with smaller n ($T > T_c$), as is clear from a comparison of the theoretical and experimental curves in Fig. 2. The experimental curves can be explained only if one assumes a transition from a phase with $n = 4$ ($T > T_c$) to a phase with $n = 8$ ($T < T_c$). Indeed, the x-ray structure data presented above suggest that the phase transition is of second order; the superlattice period can therefore change only by an integral factor,[13] i.e., phase transitions with 2 → 4, 4 → 8, etc., can occur but those with 2 → 3, 4 → 6,... are disallowed. Moreover, it was shown in Refs. 5, 6 that at room temperature, the quinoline molecules in Pb_2I–quinoline are ordered with period $4a_0$, i.e., we have $n = 4$ in the high-temperature phase. Finally, the agreement between the experimental and theoretical excitation spectra is best if we substitute into (2) and (3) the values $E_c = 1.6$ eV and $E_g = 2.3$ eV for the width of the conduction and forbidden bands taken from Refs. 14 and 15, provided we take $\delta = 0.05$ eV and assume that all the subbands have equal widths, i.e., $2\Delta_v = 0.1$ and 0.2 eV, $2\Delta_c = 0.15$ and 0.3 eV for $n = 8$ and $n = 4$, respectively (cf. Fig. 2). We note that for these parameter values, the tops of the first three valence subbands lie at a distance of 2.3, 2.45, and 2.6 eV below the bottom of the first conduction subband, respectively, while the distance from the bottom of the second conduction subband to the top of the first valence subband is equal to 2.5 eV (the distances between the other subbands are greater). We will need these values when considering the luminescence spectra.

The above model for describing the electron spectrum for PbI_2–quinoline and how it changes during the phase transition must also be consistent with the luminescence spectra. Indeed, when a miniband spectrum is present, one would in principle (at $T = 0$ K) expect to observe luminescence associated with electron transitions from the bottoms of the conduction subbands to the tops of the valence subbands. For $T \neq 0$ K, one will of course observe only the lowest-energy transitions between the subbands with the smallest indices i, because the probability for a nonradiative transition into a lower subband increases with the energy of the excited electronic state.[16] It is therefore natural to assign the luminescence at 540 nm (2.3 eV) and 510 nm (2.45 eV) to transitions from the bottom of the first conduction subband to the top of the first and second valence subbands, respectively.[2)] This assignment is supported by the luminescence spectrum for Pb_2I–quinoline found at $T = 4.2$ K in Ref. 18 (see Fig. 3). This spectrum clearly reveals luminescence bands at 2.5 and 2.6 eV which are "smeared out" at higher temperatures; they correspond to transitions from the bottom of the second conduction subband to the top of the first valence subband and from the bottom of the first conduction subband to the top of the third valence subband. Finally, further support for our interpretation of the luminescence bands is provided by the way the luminescence spectrum changes as T passes through T_c. Indeed, during the transition from the $n = 8$ to the $n = 4$ phase the gaps between the subbands with indices $2k - 1$ and $2k$ disappear ($k = 1,2,3,4$); one thus expects that the luminescence due to transitions from conduction subbands $2k$ and into valence subbands $2k$ should disappear also. As anticipated, Fig. 3 shows that the luminescence in the 2.45 eV band disappears when $T > T_c$ (this luminescence is associated with a transition into the second valence subband).

We have thus shown that a low-temperature phase transition in which the quinoline superlattice period doubles from $a = 4a_0$ to $a = 8a_0$ occurs in PbI_2–quinoline. The detailed mechanism for the phase transition remains unclear. It could involve a redistribution[3] or ordered alignment[19] of the quinoline molecules; alternatively, the transition might be of the "displacement" type. Analysis of the far-IR vibrational spectra for this compound will be crucial in deciding this question.

We note that our work indicates that luminescence and absorption spectra can be used to identify the nature of transitions that change the superlattice period and to estimate the parameters of the electron miniband spectrum.

It should be noted that the technique used above for obtaining intercalation materials with a miniband spectrum is considerably simpler than the conventional method, in which epitaxial layers must be grown with extreme precision.[20] In addition, the variety of donor molecules that can be incorporated and the range of layered semiconductor host crystals are virtually unlimited, so that it should be possible to produce superlattices with a wide range of properties.

We are grateful to V. V. Eremenko for his interest in this work and for a fruitful discussion.

[1)] The simplified dispersion law (1) is justified because the principal contribution to the absorption peaks comes from the subband edges, which are correctly described by (1). Indeed, if we assume for instance that the lattice period doubles ($n = 1 \rightarrow n = 2$) then the dispersion law cos pa_0 becomes $\pm(\delta^2 + \Delta^2 \cos pa_0)^{1/2}$ (Ref. 10), which agrees near the edges with the dependence $\pm\delta \pm (\Delta/2)\cos 2pa_0$ used in (1).

[2)] The broad luminescence band at 580 nm (Fig. 3) is due to luminescence from the singly charged Pb^+ ion and is also present in the starting PbI_2 crystal.[17] We note that the width 2.3 eV of the forbidden band for PbI_2–quinoline is the same as for the starting PbI_2 crystal. This justifies the use of the rigid band model, which postulates that the intercalated quinoline molecules in the van der Waals interstices form a superlattice and split the bands into subbands (thereby producing a miniband structure) without altering the basic band structure of the PbI_2. This conclusion is consistent with the discussion in Ref. 5, where the rigid band model was used successfully to describe several experimental results for PbI_2 intercalation compounds.

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Translated by A. Mason