

Comments

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Comment on "Evolution of intermediate excitons in fluid argon and krypton"

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In a recent paper Laporte *et al.* [Phys. Rev. B **35**, 6270 (1987)] conclude that a quantum-defect method which we introduced does not seem to describe appropriately valence excitons in rare-gas solids. However, their study refers to fluids, and the results depend on density fluctuations, which were not considered in our model. In related works Bernstorff *et al.* determine experimentally accurate energy gaps in rare-gas solids, and discover term-value–band-gap-energy linear correlations for solid rare-gas excitons. In both works they state that the quantum-defect method does not apply. However, our analysis of their findings supports a different point of view.

In a recent paper Laporte *et al.*¹ study the evolution of intermediate excitons in fluid Ar and Kr. They refer to a previous theoretical work by Resca and Resta,² based upon a quantum-defect method and a nonstructural approach, as one of the "numerous attempts to describe excitons in terms of their related atomic transitions." Also in view of other recent works to which they refer,^{3,4} Laporte *et al.* conclude that "the quantum-defect method in its present form does not seem to be the appropriate way to describe valence excitons in rare-gas solids."

At the time Ref. 2 was published we did not specifically concentrate on the findings of Laporte and Steinberger in fluid Xe,⁵ which have been subsequently confirmed for fluid Xe, Kr, and qualitatively also for Ar.^{6–8,1} According to these papers, due to density fluctuations in fluids, some of the atoms are in a gaslike environment, whereas other atoms are in an environment where the local density and number of nearest neighbors are sufficiently similar to the conditions in the liquid. As a result, distinct atomic and excitonic absorption bands are observed in fluids at the same time. In Ref. 2 we qualitatively described a continuous transformation from atomic to exciton levels during a uniform transition from gas, to liquid, and to solid. The emphasis was on the fact that our theory is "nonstructural," in the sense that it is not essentially based on the crystal structure and the corresponding band structure of the solids in \mathbf{k} space, as previous theories have been. Solid-state effects are introduced solely through the exciton reduced effective mass m^* and the dielectric constant ϵ_0 of the medium, which is essentially a smooth function of the density alone. Since the concepts of m^* and ϵ_0 may be retained in a uniform liquid phase, our nonstructural theory of excitons may

also be retained in such cases. In fact, excitons are observed in rare-gas liquids just as in solids, and the nonstructural point of view is consistent with the results summarized in the second paragraph of the paper by Laporte *et al.*¹ On the other hand, we did not address in Ref. 2 the problem of density fluctuations in fluids. Perhaps that could be tackled by studying quantum-defect electronic excitations in different clusters statistically weighted. Certainly the problem is more challenging and beyond the framework and the scope of our original nonstructural formulation.

Recently, Bernstorff and Saile³ have been able to accurately determine the energy band gaps of solid Xe, Kr, Ar, and Ne by an experimental technique combining synchrotron radiation with a dye laser. In their analysis of the data they compare the corresponding experimental gap result in solid Ne, $E_G^{\text{expt}} = 21.48_{-0.08}^{+0.04}$ eV, with a constant-quantum-defect least-squares fit of the exciton transition energies, including the $n = 1$ transition, which yields $E_G^{\text{QD}} = 21.61(\pm 0.08)$ eV, and the Wannier-formula fit which excludes the $n = 1$ transition, yielding $E_G^{\text{W}} = 21.51(\pm 0.05)$ eV. Given the high accuracy of their experimental values, Bernstorff and Saile conclude that the quantum-defect method seems not to be applicable to solid Ne, at least not with a constant quantum defect, whereas the Wannier formula is. We recall that the quantum defect for the $n = 1$ level is the one which deviates the most from the asymptotic limit, both in the solids and in the free atoms.^{2,9} This is expected, because the $n = 1$ state is the most localized and affected by the specific deviations of the short-range potential from the Coulomb form. By fitting the $n = 1$ level and the higher excited levels with a constant quantum defect, a slightly imprecise determination of the energy gap may occur. In

Ref. 2, however, by taking the theoretical exciton binding energies of the nonstructural approach with $m^* = 0.8$ and nonconstant quantum defects, and by fitting them to the experimental exciton transition energies by means of a slightly different procedure which better represents the higher levels, we determined an energy gap $E_G = 21.52$ eV (third column block in Table I). That is within the accuracy of the present experimental gap value, although the experimental exciton transition energies which we used at that time may not be as accurate as the current ones. In any event, the remarkable fact is that even the constant quantum-defect fitting can include rather precisely the $n = 1$ level together with the $n \geq 2$ levels, whereas the Wannier formula dramatically underestimates the binding energy of the exciton ground state in solid Ne by approximately 1 eV, that is, about 30%. Furthermore, the constant quantum-defect fitting and the Wannier formula predict substantially different values for the exciton reduced effective masses: 0.8 and 0.56 electron masses for solid Ne, respectively (Table I in Ref. 2). The quantum-defect value is more reasonable for a strong insulator such as solid Ne, and agrees with band-structure calculations.^{10,11} However, definitive experimental values are not available. From the theoretical point of view the Wannier formula is simply the hydrogenic result, which applies exactly only to a Coulomb potential everywhere. In solid Ne, because of weak interatomic interactions and low screening, we expect substantial effects due to deviations of the central-cell potential from the Coulomb form. The analytical study of the radial Schrödinger equation and the behavior of the corresponding logarithmic derivatives leads naturally to a quantum-defect formula, just as it is required in the well-known free-atom case.

There is no question that a more accurate experimental determination of the energy gaps and the exciton transitions in rare-gas solids is crucial to the testing and development of the theoretical model. At present, given the fact that the Wannier formula (a) completely fails to describe the exciton ground state, (b) apparently fails to describe the excited states as far as the effective mass is concerned, and (c) is based on a purely hydrogenic model which cannot be sufficiently justified, we conclude that it is not adequate to describe valence excitons in solid Ne. On the other hand, the quantum-defect formula appears to be satisfactory in all those respects. The gap prediction for a constant quantum defect appears to be slightly inaccurate (only by 0.6% in solid Ne, while in agreement with the quite accurate experimental new data for all the other rare-gas solids³), but that can be theoretically understood, and improvements are possible when quantum defects are more precisely calculated.

Recently, Bernstorff *et al.*⁴ have also discovered remarkably accurate linear correlations of the term value (i.e., binding energy) and band-gap energy for excitons in the solid-rare-gas series, completely analogous to the term-value–ionization-energy linear correlations which have been established for atomic and molecular Rydberg states. That appears to be a striking confirmation of the validity of the quantum-defect model as applied to valence excitons in rare-gas solids. However, Bernstorff

et al. again state that “it is not possible to apply the quantum-defect model to solid-rare-gas excitons if one assumes constant quantum defects.” They point out that the slopes and intercepts of the correlations in the solid-rare-gas series differ greatly from those in the rare-gas atomic series, and “conclude that the excitons of rare-gas solids do not possess atomic parentage, at least not in any simple, perturbational sense.” The quantum-defect and nonstructural approach which we introduced⁹ does not imply that. In fact, it is not an attempt to describe excitons just in terms of their related atomic transitions. What we did was to solve first the radial Schrödinger equation for the free atoms, fitting the short-range potential so as to reproduce the experimental atomic transitions. When the atom is in the solid matrix we assume that the short-range (central-cell) potential is not affected. On the other hand, the Coulombic tail becomes screened by the solid dielectric constant ϵ_0 , and the electron mass is replaced by the solid reduced effective mass m^* . We then solve the corresponding radial Schrödinger equation with these parameters. If ϵ_0 and m^* are relatively close to unity, as is the case for solid Ne, we naturally obtain exciton energies which are relatively close to the corresponding atomic energies. In fact, the quantum defects in solid Ne turn out to be about 0.5,⁹ which is relatively close to the gaseous Ne values of about 0.7. At the other end of the series, solid Xe has $\epsilon_0 = 2.217$ and $m^* = 0.34$, yielding an effective Rydberg $m^*/\epsilon_0^2 = 0.07$ times smaller than the free-atom value. Naturally the exciton levels in solid Xe lose any resemblance to the corresponding atomic transitions, and in fact the quantum defects in solid Xe turn out to be one order of magnitude smaller than in the free Xe atom.⁹ That simply reflects the fact that all the exciton envelope functions become so extended (due to the relatively strong screening and light mass) in solid Xe that the (atomic) short-range potential hardly matters, and the limit of the conventional effective mass theory is recovered (Wannier formula). Ar and Kr present intermediate situations between Ne and Xe. What is remarkable is that the quantum-defect and nonstructural approach describes simply and effectively all exciton levels, including $n = 1$, in the whole solid-rare-gas series, ranging from the atomic to the effective-mass limits. Therefore, we do expect that the slopes and intercepts of the correlations of Bernstorff *et al.* differ greatly in the rare-gas atomic series and in the solid-rare-gas series: towards one end of the latter series (solid Xe) the exciton levels and their quantum defects become completely different from the corresponding atomic values.

Bernstorff *et al.*⁴ state that the slopes and intercepts of the correlations in both rare gases and rare-gas solids are governed by the non-Coulombic portion of the total potential. Actually, the Coulombic part of the potential is screened by different dielectric constants in the solid series, and that has the major influence on the solid series correlation slopes and intercepts: the quantum defects increase from Ne to Xe in the free-atom series, whereas they greatly decrease in the corresponding solid series.⁹ However, because of the increase in the dielectric constant from solid Ne to Xe, the slopes of the correlations turn out to be positive in the solid series from Xe to Ne,

just as they are in the free-atom series. Another consequence of the different screening in the Coulombic parts of the potentials in the solids is that the limiting value of the correlation slope at high principal quantum numbers n is expected to vanish in the free-atom series, but to remain positive and finite in the solid series. The reason is that for n larger and larger the effect of the constant quantum defect becomes smaller and smaller, and the limits of hydrogen for free atoms and Wannier for solid excitons are eventually reached. In those limits the binding energies (term values) are the same (hydrogen) for all free rare-gas atoms, yielding a vanishing slope in the correlation. On the other hand, the binding energies still increase at large n from solid Xe to solid Ne because the effective Rydbergs do so, and that yields a limiting positive and finite slope in the solid series correlation. We also point out that the correlation slope is extreme for small n because the quantum defect has its largest effect at small n , even when considered constant, i.e., independent of n (for the solid series the different effective Rydbergs still play a major role). Therefore, the term-value–band-gap-energy linear correlations for solid-rare-gas excitons are consistent in every respect with the quantum-defect model, even in the approximation of constant (n -independent) quantum defects.¹²

The band structures of solid Ne, Ar, Kr, and Xe are substantially different in many respects, such as bandwidths, ordering of the critical-point energies, etc., and are not related to each other in any “linear” way.^{11,13} Yet the observed term-value–band-gap-energy correlations for excitons in the solid-rare-gas series are remarkably linear, just as they are in the free-rare-gas-atom series, where no “band structures” occur. This appears to be a substantial confirmation of the validity of a non-structural approach to excitons in solid rare gases, and in

particular of our model, in which the only differences between the gas and solid Hamiltonians are the effective masses and the dielectric constants in the Coulombic parts of the potentials. The presence of these parameters is clearly evident in the exciton spectra, while no other band-structure detail is essential within a relatively high degree of accuracy, at least as far as the energy spectra are concerned.

When we first introduced the quantum-defect and non-structural approach for valence excitons in rare-gas solids Saile and Koch described it as a “remarkable progress in describing the whole exciton series for all rare-gas solids.”¹⁴ In light of current developments this point of view is being reconsidered. Laporte *et al.*¹ traditionally describe Wannier excitons, “intermediate” excitons, Frenkel excitons, and atomic transitions as fundamentally different and unrelated physical entities in the various rare-gas phases. We still believe that the quantum-defect and nonstructural approach provides a unifying framework which is basically correct. Particularly, the discovery by Bernstorff *et al.*⁴ of remarkably accurate term-value–band-gap-energy linear correlations for all principal quantum numbers in the whole solid-rare-gas series, just as in the whole rare-gas atomic series, seems to confirm a close relationship between all those excitations as we proposed. Generally, the recent findings and considerable progress made in Refs. 1, 3, and 4 indicate, in our view, that quantum-defect and nonstructural ideas are very much alive and well, and they are here to stay.

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¹²The discussion in this and the preceding paragraph should clarify some statements about our method made by Bernstorff *et al.* (Ref. 4), in particular, in the footnote on page 163. We believe that it is indeed reasonable to assume the same non-Coulombic (short-range) potentials in the free atoms and in the solids, and there is no contradiction in obtaining non-atomic quantum defects for the solids. That depends strongly on the different screening in the Coulombic parts of the potentials in the solids, and on the different effective masses.

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