Intermediate and Wannier Excitons in Fluid Xenon

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Reflectivity spectra of MgF_2–fluid-xenon interfaces obtained for a wide range of densities revealed that the $n = 2$ Wannier exciton starts to appear at densities above 400 amagat (1 amagat of density for xenon corresponds to 2.7067×10^{19} atoms/cm^3). The $n' = 1$ exciton appears at densities above about 100 amagats on the low-energy side of the parent $5p^56s$ $[K = \frac{1}{2}]$ atomic state. The occurrence and evolution of these bands and of the previously reported $n = 1$ band with density are discussed with use of conductivity relaxation times obtained by Huang and Freeman.

The possible existence of Mott-Wannier excitons in liquids was discussed in 1966 by Rice and Jortner[1]; they pointed out that in liquid rare gases there were high chances to observe such excitons. Beaglehole[2] obtained experimental indication of Wannier excitons in liquid xenon; this was confirmed by Asaf and Steinberger.[3] Trapped Mott-Wannier excitons in doped rare-gas solids and liquids were extensively investigated.[4,5] Experimental indications for the existence of Frenkel excitons in molecular liquids were brought forward by several authors.[6-8] This Letter deals with the minimum conditions necessary for the appearance of three different free excitons and thus it is closely related to the problem of energy-band formation in disordered systems.

In a previous publication by two of the present authors[9] the transition from the ground state to the first excited state was studied as a function of the density in fluid (including liquid) xenon. In the low-density gas, this excited state is the $5p^56s$ $[K = \frac{3}{2}]$ atomic state corresponding to the 146.96 nm resonance line; at densities of about 100 amagats, this line is considerably broadened and shifted. At about 180 amagats, a further band appears near the low-energy edge of this peak. The new band increases in height with density, remaining distinct of the broadened atomic band. The new band represents an excitonic state in the fluid that corresponds to an "intermediate" exciton in the solid: It can be described as the $n = 1$ state of an (observed) Wannier exciton series or as a Frenkel exciton related to the first excited atomic state. Evidence for the evolution with increasing density of two more exciton states (one intermediate exciton and one Wan-

nier type) in the fluid will be presented here. Results for the density range 1–100 amagats and their interpretations were published previously[10]; that paper also deals with the experimental setup in St. Etienne and shows the absence of wall effects.

Figure 1 presents a set of reflection spectra for fluid-xenon–MgF_2 interfaces for various densities between 80 and 475 amagats. At the lowest densities the main features are peaks appearing at about 8.4, 9.6, and 10.4 eV; these correspond to the transitions associated with the atomic levels $5p^56s$ $[K = \frac{3}{2}]$, $5p^56s$ $[K = \frac{1}{2}]$, and $5p^55d$ $[K = \frac{3}{2}]$, respectively. Comparing the lowest densities [Figs. 1(a) and 1(b)] the most important feature seen is the very asymmetric broadening of the 9.6 eV band in Fig. 1(b). This broadening is due to the appearance (at 100 amagats) of a further band just below 9.6 eV; it corresponds to the $n' = 1$, $\Gamma([\frac{1}{2}])$ exciton band. At densities higher than 180 amagats, the above-mentioned band next to the 8.4-eV band sets in, at about 8.2 eV; this corresponds to the $n = 1$, $\Gamma([\frac{3}{2}])$ exciton in the solid.[9] Above 400 amagats, an extra band at 9 eV is also present, corresponding to the $n = 2$ exciton in the solid. The extra bands increase in height with density, with the $n = 1$ and $n' = 1$ bands becoming stronger than the neighboring "atomic" peaks. In fact, at higher densities the nearest "atomic" peak cannot even be discerned directly under the wing of the $n' = 1$ band. The growth of the $n = 1$ exciton band in comparison with the neighboring transition associated with the $5p^56s$ $[K = \frac{3}{2}]$ atomic level is illustrated in Fig. 2 for a wide range of densities. The evolution of the other two exciton bands was also followed up to the triple point den-
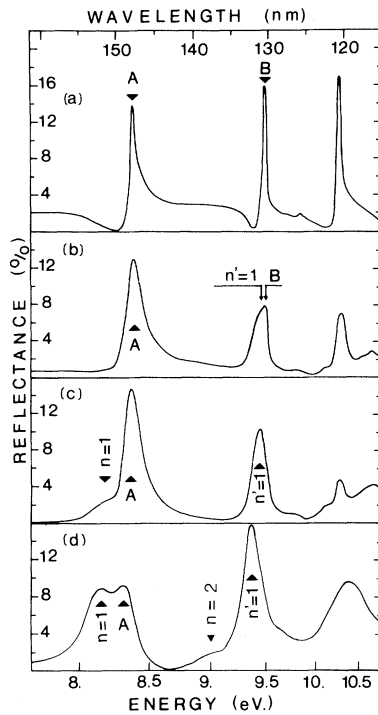
FIG. 1. Reflectances of xenon-MgF_2 interface at four densities: (a) 80 amagats, 298 K; (b) 170 amagats, 298 K; (c) 250 amagats, 298 K; and (d) 457 amagats, 200 K. Marker A denotes the position of the transition derived from the $5p^5 6s$ $[K = \frac{3}{2}]$ atomic state; marker B, that corresponding to $5p^5 6s$ $[K = \frac{1}{2}]$.

FIG. 2. Evolution of the $n = 1$, $\Gamma([\frac{3}{2}])$ exciton peak near the band originating in the atomic transiton $5p^5 6s$ $[K = \frac{3}{2}]$. The ordinate represents the ratio $R_{exc}/(R_{exc} + R_{at})$, where R_{exc} is the maximum reflectance (MgF_2/Xe) of the excitonic peak and R_{at} the maximum reflectance of the "atomic" peak.

sity. In fact, we based their assignment as given above on this evolution and on the changes of the respective exciton positions in the solid with density. It has been namely shown[11] that the triple-point positions of these bands agree very well with those expected by taking into account the density change at the solid-liquid phase transition. The changes with density around the 10.4-eV band are more complicated, probably because of the closeness of different atomic levels in this region ($5d$ $[K = \frac{3}{2}]$, $7s$ $[K = \frac{3}{2}]$, $5d$ $[K = \frac{1}{2}]$) and a possible contribution of the $n' = 2$ Wannier exciton. A detailed discussion and analysis of the behavior of the reflectivity in this region will be published shortly.

In Ref. 9, the evolution of the $n = 1$ exciton in the dense fluid was attributed to density fluctuations. A criterion for the appearance of an exciton was formulated, namely that the excited atom should be in a cluster due to fluctuations which is larger than a certain minimum volume, V_0, that includes at least N_0 atoms. It was shown that for the appearance of this exciton $N_0 = 10$ and $V_0 = 1.5$
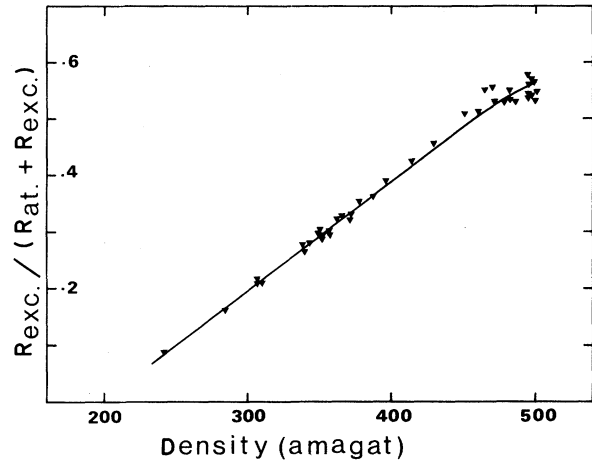
$\times 10^{-21}$ cm^3.

The difference in the densities at which the two partially Frenkel-type excitons ($n = 1$ at 8.2 eV and $n' = 1$ at 9.5 eV) appear seems to be due to the difference of the effective average radii $a([\frac{3}{2}])$ and $a([\frac{1}{2}])$ of the parent atomic states, $5p^5 6s$ $[K = \frac{3}{2}]$ and $5p^5 6s$ $[K = \frac{1}{2}]$, respectively. $a([\frac{3}{2}])$ and $a([\frac{1}{2}])$ were estimated as usual for Rydberg states, by assuming a hydrogenlike model and assigning effective principal quantum numbers.[12] This leads to the estimation $a([\frac{3}{2}]) = 0.272$ nm and $a([\frac{1}{2}]) = 0.418$ nm. It follows that the local density needed for effective energy transfer and the formation of the $n' = 1$ exciton should be markedly lower than for the formation of the $n = 1$ exciton. In fact, the average interatomic distances calculated for the density thresholds (100 and 180 amagats, respectively) agree within an accuracy of 15% with the effective average diameters calculated in the above manner.

While the radii of both the $n = 1$ and $n' = 1$ excitons are of atomic dimensions, the $n = 2$ exciton has a Bohr radius of 1.0–1.2 nm, depending on the density. Accordingly, there is a further condition on the minimum volume of the sustaining cluster: It has to be of the order of magnitude of the sphere whose radius is equal to that of the exciton orbit, i.e., at least 4×10^{-21} cm^3. Since this volume is larger than that of the cluster sustaining the $n = 1$ and $n' = 1$ excitons, it is not surprising that the $n = 2$ exciton appears at a higher den-

sity than these two. For the $n = 2$ Wannier exciton two necessary conditions must also be fulfilled: (a) From the indeterminacy principle, $\Delta E \geq h/\pi\tau_c$; (b) from the cyclotron condition,[1] $\omega\tau_c > 1$. ΔE denotes the full width at half height of the exciton band; h, Planck's constant; and ω, the classical angular frequency of the electron. According to basic considerations[1,13] for the extended orbits of Wannier excitons, it is justified to equate τ_c with the relaxation time of the electrical conductivity. By using the data of Huang and Freeman[14] on the mobility and by assuming an exciton reduced effective mass of $m^* = 0.35m$ (m being the mass of the free electron) as in solid xenon,[15] one obtains at 400 amagats $h/\pi\tau_c = 3.5 \times 10^{-3}$ eV (compared with $\Delta E \approx 0.12$ eV) and $\omega\tau_c = 140$. Thus the necessary conditions for the appearance of the $n = 2$ exciton are amply fulfilled; it seems that further restrictions, probably connected with density fluctuations, prevent its appearance at lower densities.

These observations strongly support the claim[9] that intermediate excitons in pure fluids are entities different from broadened and shifted atomic or molecular states. They are the first results on the evolution of the Mott-Wannier excitons in any pure noncrystalline material. The remarkable simplicity of the electronic properties of condensed xenon is clearly illustrated.

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Plasmon Dispersion in Aluminum-Magnesium Alloys

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Dispersion measurements of the volume plasmon in Al-Mg alloys show that the dispersion coefficient α defined at low wave vectors k does not exhibit the expected free-electron—gas behavior, whereas this is the case for the generalized α at higher k. Optical reflection measurements support the suggestion that low-lying interband transitions influence the dispersion in the small-k regime.

The dispersion $\omega(k)$ of bulk plasmons in free-electron metals provides an important test on the dynamical effects of exchange and correlation, which go beyond the random-phase approximation (RPA). Recent dispersion measurements[1-3] in aluminum showed an unexpected nonquadratic dispersion.[4] Sturm[5] predicted that this should be a universal effect in all nearly-free-electron metals. He pointed out, in agreement with Bross,[6] that the theoretical dispersion that follows from