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Reflectance measurement of the VUV spectrum of solid xenon and its temperature dependence up to the triple point

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Résumé. — Le facteur de réflexion du xénon solide dans la région 6,2-10,8 eV a été mesuré en valeur absolue avec précision. Le solide est étudié en cellule fermée (fenêtre prismatique en fluorure de magnésium) dans le domaine de température 80-160 K. La qualité des résultats a permis notamment de mettre en évidence le terme $n = 4[\Gamma(3/2)]$ de la série excitonique et de suivre son évolution jusqu'à sa disparition vers 135 K.

Abstract. — Accurate solid xenon reflectance measurements in the energy range 6.2-10.8 eV are reported. The solid, confined in a closed cell (MgF_2 prismatic window), has been studied in the temperature range 80-160 K. The detailed, reliable results allowed the clear observation of the $n = 4[\Gamma(3/2)]$ term of the excitonic series; its evolution was followed up to 135 K where it disappears.

1. Introduction. — Since Baldini's paper [1], extensive studies on solid rare gas excitonic spectra near the onset of valence band transitions have been performed. Investigations have been done mostly on thin films (reflection or transmission), and also in a closed cell with LiF or MgF_2 windows (reflection). Most of these studies have recently been critically reviewed by Sonntag [2]. From this compilation, important discrepancies which can reach a factor of two for absolute peak reflectivities can be noted. Furthermore these discrepancies change throughout the spectrum. The available optical constants are consequently questionable despite the great care used for many of the experiments reported. It clearly illustrates the quasi-impossibility of properly and simultaneously solving for thin solid films the following experimental difficulties :

- surface contamination,
- surface roughness (scattered light...),
- crystal defects of evaporated thin films,
- interference effects,
- sublimation of the sample when examined in a large temperature range,
- thickness measurement for absolute scaling in transmission measurements,

— selective reflection losses in transmission measurements,

— back reflected light from the substrate in reflection experiments,

— absolute scaling of reflectivity.

The purpose of the present letter is to show that for a certain class of experiments, due to the transparency limit of VUV windows, careful closed cell experiments lead to accurate results. Measurements on xenon in the energy range 6.2-10.8 eV, including the excitonic bands related to $6s[3/2]$, $6s[1/2]$, $5d[3/2]$ atomic lines are reported for the case of MgF_2 as window material.

2. The experiments. — The experiments are performed with a double beam spectrophotometer using a deuterium source. The details of the set up including a computer (PDP 11-03) have been developed elsewhere [3]. The absolute scaling of the xenon reflected spectrum is established from the reflectance $R_0(E)$ of the empty cell *via* the computer, using the *a priori* known values :

$$R_0(E) = \left(\frac{n'(E) - 1}{n'(E) + 1} \right)^2$$

where $n'(E)$ is the refractive index of the magnesium fluoride window at the energy E [4]. Although the refractive index is only known at room temperature,

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systematic study of the temperature effect on $R_0(E)$ has been done. It turns out that the reflectivities given in this paper can be estimated to be accurate within 2 or 3 % for $E < 10$ eV i.e. for all the main reflectance peaks. The experimental set up was originally developed for quasi-normal (1.8°) incidence reflectance studies on liquid and gases under pressure [5]. Nevertheless, without any change in the optical cell, it has been possible to study solid xenon in the temperature range 80-160 K (triple point : $T = 161.391$ K, $P = 0.816$ bar [6]).

The solid is formed by cooling down the optical cell filled with liquid xenon to obtain good crystallization [7]. Freezing either near the triple point or with an overpressure of ten bars was tried to test the change in reflectivity with thermodynamical conditions of solid formation. Similar, highly reproducible results have been obtained. Actually, as illustrated in figure 1, phase changes (solid $\leftrightarrow$ liquid) observed at constant energy, give back the $n = 1$ [$\Gamma(3/2)$] exciton peak reflectivity of xenon with a reproducibility of 1 %.

Fig. 1. — Observed reflectance R (ratiometer output) of Xe/MgF_2 interface at constant energy ($n = 1$ exciton peak position) during temperature (T) cycles (~ 1 K amplitude around 161.4 K) including solid-liquid transition. The reference signal of the double beam system also appears on the figure.

If we add to this striking result the following observations :

- i) no annealing effect was observed during the solid xenon experiments,
- ii) a very low reflectivity, which implies *a fortiori* a low level of scattered light, is observed around 8.64 eV (see § 3),

we conclude that the experimental conditions are very good. During the experiments an overpressure of a few bars was maintained in the system. Furthermore, as solid xenon remains soft [7] in the temperature range investigated, reflectance measurements were performed without any separation between the xenon and the window due to the difference in the expansion coefficient. Such an effect would in fact have been immediately observed by a reflectivity change and irreproducibility.

3. **Results.** — Figure 2 gives an example of the direct analogic recording of the data simultaneously computerized. The intensity level is high enough to work without any averaging cycle. An essential point is the very high peak reflectivities observed. Such a result, differs considerably from the work reviewed in reference [2]. Recently Kink *et al.* [8] observed $n = 1$ [$\Gamma(3/2)$] peak reflectivities of 60 to 80 % depend-

Fig. 2. — Direct recording of the Xe/MgF_2 interface reflectance $R(\%)$ vs. energy obtained at 120 K, showing the different excitons observed (a : $n = 1$; b : $n = 2$; c : $n = 3$; d : $n = 4$; e : $n' = 1$). The monochromator provides a linear wavelength scale (λ). Note the sensitivity change at 143.7 nm.

ing on the quality of the crystal (LiF window). Our results confirm in a quantitative, reproducible way those of the latter authors. In figure 3 we give the temperature dependence of the main peak reflectivities. Such high reflectivity values at temperatures approaching the thin solid films experiments clearly indicate that reflection losses must be taken into account to obtain absorption from transmission measurements.

Another feature apparent in figure 2 is the systematic observation of the $n = 4$ [$\Gamma(3/2)$] exciton up to 135 K. An example of the computerized data (no

Fig. 3. — Reflectance maxima versus temperature for the main solid xenon excitonic peaks observed.

averaging cycles) in the region of the $n = 3,4 [\Gamma(3/2)]$ peaks is given in figure 4. Reflectance peak positions, including the $n = 4$ exciton in the temperature range of observation, are reported in figure 5. The energy calibration is provided by recording simultaneously the deuterium and the xenon spectra. The absolute values reported are reproducible to within 0.005 eV for $n = 2, 3, 4 [\Gamma(3/2)]$, and 0.01 eV for $n = 1 [\Gamma(3/2)]$, $n' = 1 [\Gamma(1/2)]$ due to the large width of the last bands. Most of the experiments are performed at a monochromator speed of 2.5 nm/min.

Fig. 4. — Detail of the digitalized raw data given by the ratiometer associated with the double beam system in the region of the $n = 3,4$ xenon excitons at 118 K.

Fig. 5. — Energy peak position versus temperature in the solid xenon spectrum.

Our results for peak positions agree well with those reported by Steinberger and Asaf [9] for $n = 1, 2$ and $n' = 1$, indicating that this parameter is rather insensitive to the window material (LiF) and to the difference in absolute reflectivities. On the other hand, our results differ somewhat for the $n = 3$ exciton : a constant value of the peak position within the above accuracy of 0.005 eV is found for $n = 3$ and 4 in the whole temperature range. This new result for these narrow bands, where the smallest spacing between reflection and absorption peaks is expected to occur, indicates that reliable optical constants (work in progress) are highly desirable : In particular different physical processes can be invoked for the peak absorption shift, depending on the nature of their evolution as outlined by Steinberger and Asaf.

An excitonic Wannier series $n = 1, 2, 3...$ is expected to fit the hydrogeniclike formula :

$$E_n = E_G - G/n^2$$

where E_n is the energy position of the corresponding exciton, E_G the energy gap between the higher valence band and the conduction band, and G the binding energy.

It is well known that the $n = 1$ exciton has to be considered as intermediate [10], so that E_G and G values have been previously determined [1, 9, 11] from $n = 2$ and 3 only.

In the present work the observation of the $n = 4$ exciton provides an opportunity to determine E_G and G from $n = 2$ and 3 and from $n = 3$ and 4 separately. For this calculation we start as usual from peak reflectivities. Table I gives the results obtained for solid xenon at 100 K. Values obtained from $n = 1$ and 2 have also been calculated for comparison.

Table I. — Energy gap E_G and binding energy G of solid xenon at 100 K from exciton peak positions.

Energy E_i of the $n = i$ exciton			E_G (eV)	G (eV)
$E_1 = 8.332$	and	$E_2 = 9.043 \rightarrow$	9.280	0.95
$E_2 = 9.043$	and	$E_3 = 9.182 \rightarrow$	9.293	1.00
$E_3 = 9.182$	and	$E_4 = 9.235 \rightarrow$	9.303	1.09
$E_2 = 9.043$	and	$E_4 = 9.235 \rightarrow$	9.300	1.02

The essential point to notice is that for the first time a good agreement between the different sets E_G , G is obtained. In particular Baldini [1] who observed some indication of a $n = 4$ exciton did not obtain agreement for it. In that case the effect of film thickness which is then comparable with the $n = 4$ excitonic radius ($\sim 60 \text{ \AA}$) may be invoked. Our values are in agreement with those available from $n = 2, 3$ in reference [9] ($E_G = 9.285 \text{ eV}$, $G = 1.0 \text{ eV}$), and with the result obtained for E_G by Asaf and Steinberger [12] from photoconductivity threshold measurements at 130 K ($E_G = 9.265 \text{ eV}$).

We do not report E_G and G values in the whole temperature range since accurate final values have to use k (absorption) peak position. A suitable Kramers-Krönig treatment to obtain reliable optical constants from R values is in progress. It will then be possible to take into account recent theoretical improvements in the excitonic model [13], successfully applied in the case of solid neon by Saile and Koch [14]. A large amount of information which is

beyond the scope of the present letter is then expected. Particular attention will be paid to the understanding of the higher energy part of the spectrum ($E > 9.7$ eV) which is not discussed here. Actually no clear assignment has been done until now in that energy range (9.7-10.8 eV), but we think that the work undertaken on gaseous [15], fluid and liquid xenon [5, 16] which is still in progress will be of use. This topic will be the subject of a forthcoming paper.

References

- [1] BALDINI, G., *Phys. Rev.* **128** (1962) 1562.
- [2] SONNTAG, B., in : *Rare Gas Solids*, eds. M. L. Klein and J. A. Venables (Academic Press, London) 1977, chap. 17.
- [3] LAPORTE, P., SUBTIL, J. L., BON, M., and DAMANY, H., *Appl. Opt.*, June 1981.
- [4] WILLIAMS, M. W. and ARAKAWA, E. T., *Appl. Opt.* **18** (1979) 1477.
- [5] LAPORTE, P., SUBTIL, J. L., ASAF, U., STEINBERGER, I. T. and WIND, S., *Phys. Rev. Lett.* **45** (1980) 2138.
- [6] CRAWFORD, R. K., in : *Rare Gas Solids*, eds. M. L. Klein and J. A. Venables (Academic Press, London) 1977, chap. 11.
- [7] VENABLES, J. A. and SMITH, B. L., in : *Rare Gas Solids*, eds. M. L. Klein and J. A. Venables (Academic Press, London) 1977, chap. 10.
- [8] KINK, R. and SELG, M., *Phys. Status Solidi* (b) **96** (1979) 101.
- [9] STEINBERGER, I. T. and ASAF, U., *Phys. Rev. B* **8** (1973) 914.
- [10] ROSSLER, U., in : *Rare Gas Solids*, eds. M. L. Klein and J. A. Venables (Academic Press, London) 1977, chap. 8.
- [11] SAILE, V., Dissertation, München (1976).
- [12] ASAF, U. and STEINBERGER, I. T., *Phys. Lett.* **41A** (1972) 19 ; *Phys. Rev. B* **10** (1974) 4464.
- [13] RESCA, L. and RESTA, R., *Phys. Rev. B* **21** (1980) 4889.
- [14] SAILE, V. and KOCH, E. E., *Phys. Rev. B* **20** (1979) 784 ; **21** (1980) 4892.
- [15] LAPORTE, P. and DAMANY, H., *J. Physique* **40** (1979) 9.
- [16] LAPORTE, P. and STEINBERGER, I. T., *Phys. Rev. A* **15** (1977) 2538.