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Ultraviolet Absorption of Solid Argon, Krypton, and Xenon*

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The absorption spectra of thin films of argon, krypton, and xenon have been measured between 20 and 50°K in the region from 1600 to 900 Å (8 to 14 eV). The spectra show: (a) strong doublets corresponding to the atomic resonance doublets, (b) lines apparently of nonatomic nature, and (c) absorption continua. The experimental results are discussed in terms of the Frenkel and Wannier exciton models and the band gaps are estimated. Reasonable agreement is found between experimental results and available theoretical predictions.

I. INTRODUCTION

EXPERIMENTAL and theoretical investigations of the electronic and optical properties of solid argon, krypton, and xenon have been reported in the last few years.[1–3] Strong absorption lines have been found by Schnepp and Dressler in the spectra of krypton and xenon investigated from 3500 to 1200 Å, but no absorption whatsoever in argon in this range.[1] The solid rare gases, bound essentially by the weak van der Waals forces and characterized by a face-centered cubic lattice of closed shell atoms, represent very simple systems. However, experimental difficulties are encountered because their optical absorption spectra lie in the vacuum ultraviolet and they are solid in vacuum only at low temperatures. The theory of electronic states in argon crystals has been developed recently by Knox[2] in terms of the Frenkel model, and by Knox and Bassani[3] who calculated the band structure of solid argon. Absorption linewidths have been also discussed for solid noble gases[4,5] and impurity states have been treated theoretically[6] and experimentally.[7]

We report here a detailed investigation of the absorption spectra of solid films of argon, krypton, and xenon from 1600 to 900 Å. A special technique, based on the use of a phosphor, was necessary to overcome the principal experimental difficulty peculiar to this region of the spectrum, i.e., the lack of any transparent material suitable for holding the thin films in vacuum. This technique and other experimental details are described in Sec. II. The absorption spectra are illustrated in Sec. III and discussed in Sec. IV in terms of existing theories of the electronic structure of the rare gas solids.

II. EXPERIMENTAL PROCEDURE

The ultraviolet radiation source used was a Hanovia quartz lamp, operated with hydrogen, which provided a line spectrum in the wavelength range of the present experiment (1650–850 Å). The hydrogen gas pressure was about 0.2 Torr and the lamp drew 450 mA at 1200 V dc. The hydrogen gas, leaking through the entrance slit of the vacuum monochromator, was removed continuously from the latter by means of an oil diffusion pump at the pressure of about 5×10^{-3} Torr. The monochromator employed a 40-cm Bausch & Lomb replica grating, blazed at 1200 Å, at normal incidence, and the dispersion was 40 Å/mm in first order. The scanning rate was 100 Å/min. Typical slit widths for the present experiment were 25 and 50 μ corresponding to 1 and 2 Å resolution, respectively. A double Dewar cryostat was attached to the exit slit housing of the monochromator and a small diffusion pump connected to the cryostat pumped the hydrogen gas, leaking from the monochromator, at a pressure of $\sim3\times10^{-5}$ Torr.

A rod of sapphire, $\frac{1}{2}$ in. long and $\frac{1}{2}$ in. in diameter, was mounted in a cylindrical hole in a copper block on the bottom of the helium reservoir, as shown in Fig. 1; the two flat ends of the rod had been previously coated with the phosphor 2,2′dioxy-1,1′-naphthaldiazine, known in Russian literature as liumogen.[8] This phosphor, which can be sublimed above 150°C, converts the ultraviolet radiation into visible (green) light with wavelength >5000 Å; the quantum efficiency of the process is almost constant in the wavelength range of this experiment.[9] The liumogen films deposited onto the sapphire rod were a few microns thick and the ultraviolet light was totally absorbed in the phosphor films. It was also observed that from about liquid-nitrogen temperature to liquid-helium temperature the efficiency of the phosphor-photomultiplier combination became about three times larger than at room temperature.

Argon, krypton, and xenon films were deposited in a few seconds on the liumogen-coated sapphire holder. A thin film was condensed on one side and a thicker film on the other side as shown schematically in Fig. 1. The

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[1] O. Schnepp and K. Dressler, J. Chem. Phys. **33**, 49 (1960); J. R. Nelson and P. L. Hartman, Bull. Am. Phys. Soc. **4**, 371 (1959).

[2] R. S. Knox, J. Phys. Chem. Solids **9**, 265 (1959).

[3] R. S. Knox and F. Bassani, Phys. Rev. **124**, 652 (1961).

[4] P. H. E. Meijer, J. Chem. Phys. **34**, 2078 (1961).

[5] A. Gold and R. S. Knox, J. Chem. Phys. **36**, 2805 (1962).

[6] A. Gold, J. Phys. Chem. Solids **18**, 218 (1961).

[7] O. Schnepp, J. Phys. Chem. Solids **17**, 188 (1961); M. McCarty and G. W. Robinson, Mol. Phys. **2**, 415 (1959); W. Weyhmann (private communication).

[8] E.g., V. S. Vavilov and K. I. Britsyn, Optics and Spectroscopy **8**, 452 (1960).

[9] D. B. Dutton and R. A. Knapp (private communication).

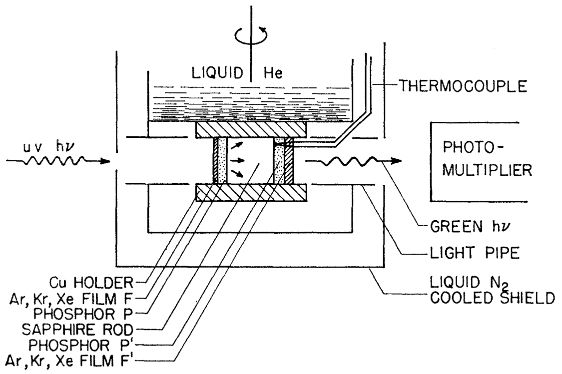

FIG. 1. Schematic representation of film holder. Note that the phosphor luminescence, excited in the layer P by the uv radiation transmitted by F, is not absorbed by the sapphire rod, P' and F'.

absorption spectra, then, refer to films whose thicknesses are the difference between the two. The reflectivity is assumed to be the same at both "thin" and "thick" films and consequently no reflection correction has to be made to the absorption spectra. The optical density at each wavelength was then given by the logarithm of the ratio of the signals (corrected for stray light) obtained when the two ends of the rod were alternatively placed in the ultraviolet beam. This technique has the advantage that it tends to cancel out the absorption due to unwanted vapors (e.g., oil, water) freezing on the rare gas films. In this arrangement, however, the rare gas film luminescence excites the phosphor luminescence and this is detected by the photomultiplier together with the phosphor luminnescence excited by the monochromatic ultraviolet light. Preliminary measurements of the excitation spectra of solid rare gases have shown that their luminescence is very weak compared with that of the phosphor and consequently the correction to the absorption spectra would be negligible. The phosphor luminescence was detected with an E.M.I. 6097S photomultiplier whose output was fed to $\frac{1}{4}$ sec Brown recorder.

The inert gases used were very pure; the impurity concentration was always less than 10^{-4}. The amount of gas needed in each deposition was estimated by measuring the pressure drop in the gas reservoir after each film had been condensed. Approximately 10^{18} atoms were introduced into the cryostat in order to obtain optical densities of about 1.5 at the absorption maxima. From geometrical considerations and assuming that all the atoms striking the cold surface were trapped, the thickness difference of "thin" and "thick" films, for maximum optical density of 1.5, was estimated to be $\sim$100 Å. The corresponding absorption coefficient, then, turned out to be $\sim 3\times10^6$ cm^{-1}. The film temperatures were measured with a Au:2.1% Co–Ag:0.37% Au thermocouple (see Fig. 1). One of the two joints was soldered with indium to a gold spot previously deposited on the sapphire surface. The measured temperature was $\sim$20°K when liquid helium was present in the cryostat.

Liquid-nitrogen cooled traps proved to be necessary to prevent oil and water vapors, which strongly absorb the vacuum ultraviolet light, from condensing on the grating and the rare gas films. Because no systematic absorption was found at photon energies lower than that of the first peak, it is apparent that the films remained "clean" during the time required by each experiment (approximately 2 h).

III. EXPERIMENTAL RESULTS

The absorption spectra of solid argon, krypton, and xenon are shown in Figs. 2–4, where the data taken at $\sim$20°K are plotted as individual points connected by a solid curve. The dashed lines show the absorption spectra at 40°K for krypton and 53°K for xenon. The energies of the resonance doublets in the free atoms are indicated by two short vertical lines.

The absorption spectrum of argon films condensed and observed at 20°K consists of a doublet with its components centered approximately at 12.0 and 12.3 eV (Fig. 2). The total width of the doublet is 0.6–0.7 eV. Compared with the atomic resonance doublet ${}^1S_0-{}^{3,1}P_1$, the absorption in the solid occurs at $\sim$0.5 eV higher energy; the energy difference between the components goes from 0.21 eV for the atom to about 0.3 eV for the solid. A rough estimate of the peak half-widths gives 0.3 and 0.4 eV, respectively, for first and second component. Another absorption band occurs at $\sim$13.8 eV; at this energy, unfortunately, the radiation intensity becomes extremely weak and the measurements are subject to rather large error. The dashed portion of the curve represents the average of a few spectra. The large linewidth and the long absorption tail, extending from

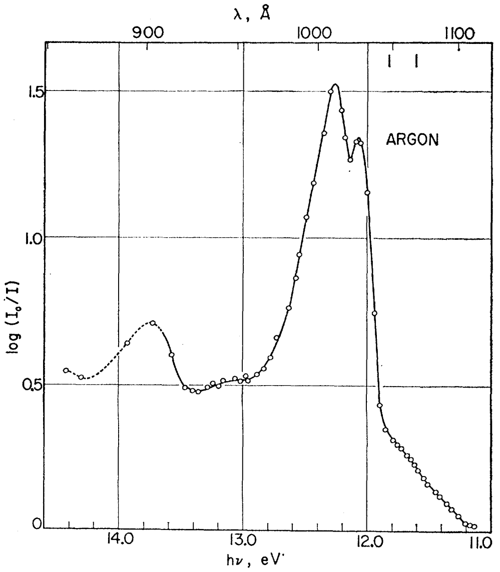

FIG. 2. Absorption spectrum of solid argon at 20°K. Bandpass 2 Å. The two short vertical lines in this and the following figures show the energy of the resonance doublets in the free atom.

TABLE I. Energies in eV of the principal absorption doublets in argon, krypton, and xenon. Widths (in eV) are given in parentheses. The last two columns give the differences (in eV) between solid and atomic absorption energies.

Element	First peak	Second peak	Triplet[a]	Singlet[a]	ΔE_1	ΔE_2
Argon 20°K	12.0 (0.3)	12.3 (0.4)	11.62	11.83	+0.4	+0.5
Krypton[b] 20°K	10.19 (0.24)	10.88 (0.21)	10.03	10.56	+0.16	+0.32
Krypton 20°K	10.17 (0.15)	10.81 (0.13)	10.03	10.56	+0.14	+0.25
Krypton 40°K	10.15 (0.19)	10.80 (0.16)	10.03	10.56	+0.12	+0.24
Xenon[b] 19°K	8.53 (0.32)	9.62 (0.2)	8.43	9.57	+0.10	+0.05
Xenon 21°K	8.36 (0.16)	9.53 (0.1)	8.43	9.57	−0.07	−0.04
Xenon 53°K	8.36 (0.25)	9.48 (0.1)	8.43	9.57	−0.07	−0.09

[a] Atomic resonance lines.
[b] Unannealed films.

11.3 to 11.8 eV on the low-energy side of the doublet, are probably caused by a high concentration of defects in the crystalline structure of the films. Annealing of the films, found successful for krypton and xenon, did not produce sharper peaks in argon. However, the temperature could only be raised a few degrees above 20°K because the argon films sublimed at higher temperatures.

When krypton is condensed and observed at 20°K two absorption peaks appear at 10.19 and 10.88 eV. These two lines, the first of which was reported by Schnepp and Dressler,[1] have a blue shift of 0.16 and 0.32 eV, respectively, compared with the atomic doublet. Their half-widths are 0.24 and 0.21 eV, respectively. At energies greater than 11 eV and up to 14 eV the absorption spectrum consists of a continuum. If the film temperature is raised to 40–50°K for 1–2 min and lowered to 20°K, then the two peaks become sharper and the energies at the maxima shift slightly to the red (Fig. 3). The peaks are now at 10.17 and 10.81 eV and their half-widths are 0.15 and 0.13 eV, respectively. On the high-energy side of the second peak new lines have appeared at 11.24, 11.48, and 11.95 eV; at $\sim$12 eV a continuous absorption begins. When the annealed film is observed at $\sim$40°K, the peaks shift to the red by a few hundredths of eV, their half-widths increase and the absorption coefficients at the peak maxima decrease. The sharper spectrum of annealed films suggests that even at low temperatures the defects, created during the film condensation at 20°K, have appreciable mobility at $\sim$40°K and that a better crystalline structure is obtained by the annealing process.

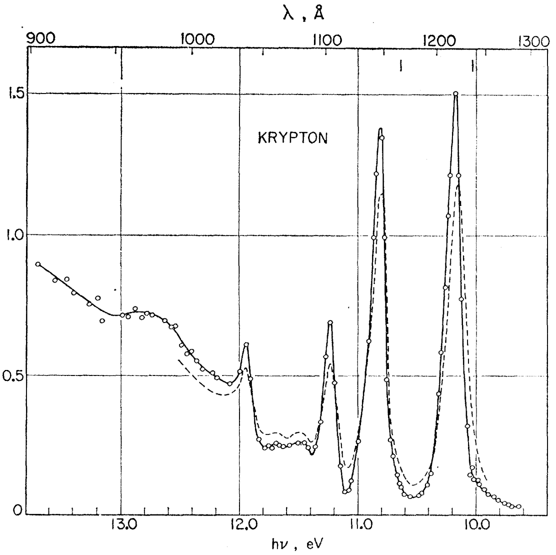

FIG. 3. Absorption spectrum of solid krypton at 20°K (annealed at 44°K), solid line, and at 40°K, dashed line. Bandpass 2 Å.

The effect of thermal treatment can be seen in Fig. 4 which shows the absorption spectra of xenon films. The solid curve of Fig. 4(a) represents the absorption spectrum of a film condensed and observed at 19°K and the dashed curve corresponds to the same film at 53°K. The two prominent peaks in the lower temperature spectrum appear at 8.53 and 9.62 eV, displaced to higher energies, with respect to the atomic resonance doublet, by 0.10 and 0.05 eV. Between the two components of the doublet, a shoulder and a bump are visible. The half-width of the first band is 0.32 eV. When the temperature is raised to about 53°K, a sharp line appears at 9.07 eV, between the two strong peaks, now appreciably sharper. The films, whose temperature has been raised to $\sim$50°K for 1–2 min, display absorption spectra, at low temperatures, similar to that of Fig. 4(b). The first peak is now at 8.36 eV and its half-width is 0.16 eV, about one half of the previous width. Other two small peaks are shown at the high-energy side of the 9.07 eV line, at 9.19 and 9.28 eV. The complex absorption structure at energy higher than 9.6 eV is slightly affected by the thermal treatment. The prominent doublet and the line at 9.07 eV have been reported together with a line on the low-energy side of the first peak.[1] The presence of lines at energy lower than that of the first peak, in both xenon and krypton, is not confirmed by this investigation.

Table I lists positions and widths (in parentheses) of the prominent absorption doublets in Ar, Kr, and Xe; also shown, for comparison, are the energies of the atomic resonance lines $^1S_0-^{3,1}P_1$ (spin-orbit doublets) and the differences between solid and atom absorption energies.

Because the rare gas films are deposited in a low-pressure hydrogen atmosphere, one might ask whether they contain trapped hydrogen. Absorption due to these impurities (e.g., the Lyman alpha) is not detected;

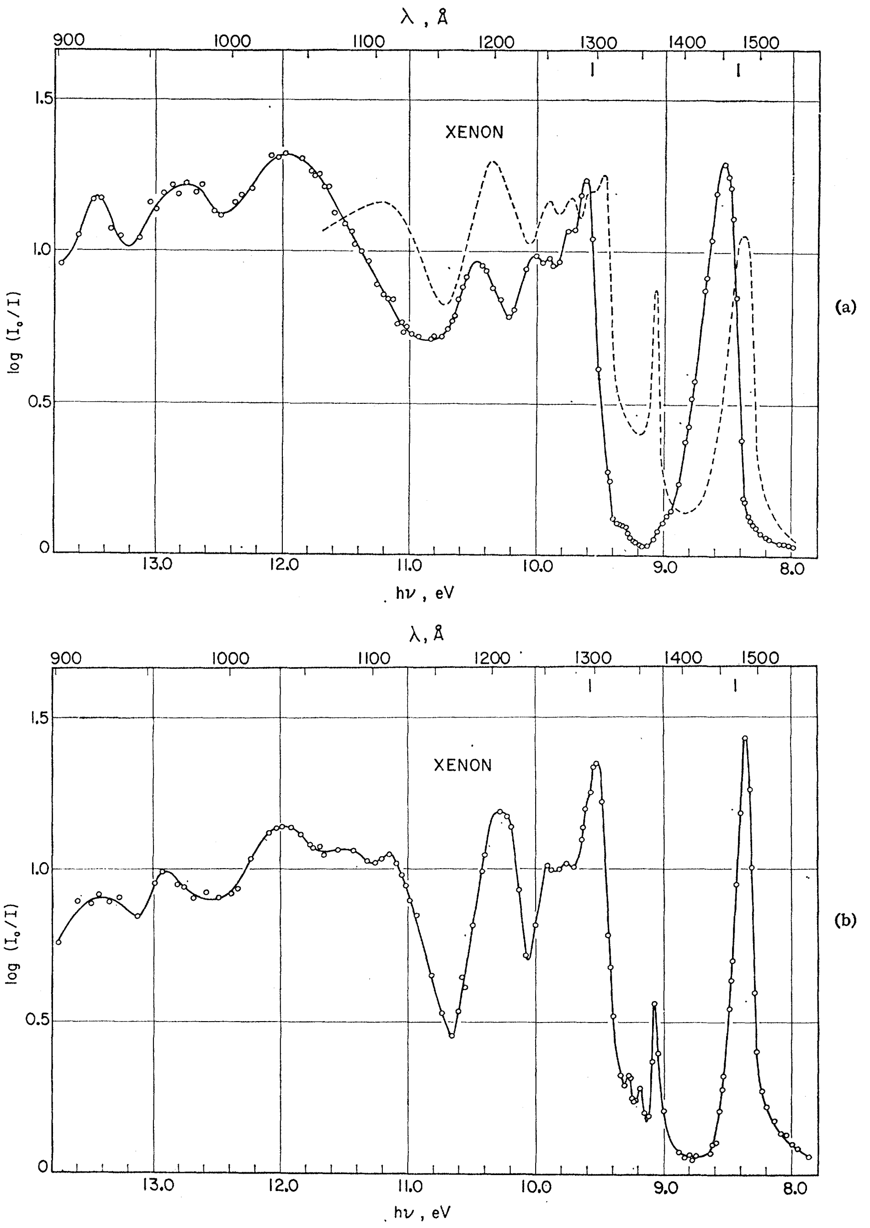

FIG. 4. (a) Absorption spectrum of solid xenon (not annealed) at 19°K, solid line, and at 53°K, dashed line. Bandpass 1 Å. (b) Absorption spectrum of solid xenon (annealed at 53°K) at 21°K. Bandpass 1 Å.

the annealing process, which would certainly favor the outgassing of hydrogen, does not remove or weaken any absorption peak. On the contrary, as seen above, new peaks appear. The possibility of hydrogen trapping, therefore, does not appear to affect our interpretation of the data as being characteristic of the pure crystal.

IV. DISCUSSION

In the theory of excitons two limiting models can be distinguished according to the "size" of the excitons, i.e., the average separation of electron and hole. In the Frenkel model one assumes that the exciton wave function is concentrated in a small region whose size is of the order of magnitude of the unit cell. The Wannier scheme, on the other hand, describes excitons having a large radius compared with the lattice constant. So far, indications are that in the inert gas solids the exciton radius is neither "small" nor "large."[2,5]

The absorption doublets in solid argon, krypton, and xenon are found at energies close to those of the atomic resonance doublets. This suggests agreement with the Frenkel picture which also predicts oscillator strengths[2] consistent, in order of magnitude, with the observed absorption coefficients. The doublets occur also in alkali halide spectra,[10] where they can be readily in-

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[10] E.g., J. E. Eby, K. J. Teegarden, and D. B. Dutton, Phys. Rev. **116**, 1099 (1959).

terpreted in terms of models closely related to the Frenkel model.[11]

As we have seen above, there appear slightly weaker absorption lines in the neighborhood of the doublets. They cannot be interpreted in the Frenkel scheme unless higher atomic transitions are abnormally shifted, from atom to solid, compared with the doublet shifts. For example, the peak at 9.07 eV in solid xenon is 0.38 eV below the closest atomic level ($^3P_0$) while the peak at 9.53 eV, apparently corresponding to the $^1P_1$ level, has a shift of only -0.04 eV. Even more disturbing is the fact that if the 9.07-eV line were due to the $^3P_0$ level, the $^3P_2$ level should also be observed on the low-energy side of the 8.36-eV ($^3P_1$) line. Both the $^3P_0$ and $^3P_2$ peaks would correspond to forbidden transitions, with the $^3P_2$ even more likely to occur. In solid krypton, absorption lines occur very close to the doublet on the high-energy side; so close, in fact, that to interpret them as greatly red-shifted higher atomic states would be somewhat inconsistent with the actual blue shift of the doublet.

The absorption doublets can also be described[12] as Wannier excitons with $n=1$, built from a spin-orbit split valence band and the lowest conduction band. This picture is not inconsistent with the Frenkel model because of the exciton's "intermediate" radius, and so the the two models give complementary descriptions of the lowest excited states. However, the Wannier model can account for the "extra lines" observed, with either of the two interpretations: (a) They correspond to Wannier excitons with $n=2,3,\cdots$, at $\mathbf{k}=0$ (Γ point) or (b) to $n=1$ excitons at some other point (e.g., L) in the Brillouin zone.[12]

According to (a), two series of Wannier excitons should appear in correspondence with the two valence bands. It is possible to estimate the binding energy G of the excitons and the energy gap E_G, between the higher valence band and the conduction band, from the equation[13]

$$h\nu_n=E_G-G/n^2, \qquad n=1,2,3,\cdots, \tag{1}$$

where $G=\mu\epsilon^{-2}$ ry, ϵ is the dielectric constant, and μ, the reduced mass of the exciton in electron mass units, is given by $\mu^{-1}=m_e^{*-1}+m_h^{*-1}$. The radii are given by $a_n=\epsilon\mu^{-1}n^2$ Bohr radii. The levels in the series of higher energy (associated with the deeper valence band) are given by an analogous equation, with a different gap energy and binding energy. In either case any two lines of the series may be used to deduce E_G and G from the spectra, but it is preferable that $h\nu_1$ not be used. This level corresponds to the exciton of smallest radius, for which the effective mass approximation is the poorest.

If the peaks at 9.07 and 9.19 eV in solid xenon are assumed to correspond to $h\nu_2$ and $h\nu_3$, respectively, E_G calculated from (1) is found to be 9.28 eV and $G=0.86$ eV. The $n=1$ energy computed with the experimental values of G and E_G is $h\nu_1=8.42$, in remarkably good agreement with the observed 8.36-eV peak. The line at 9.28 eV does not fit the series for $n=4$.

The same calculations performed for krypton give $E_G=11.67$ eV and $G=1.73$ eV when $h\nu_2=11.24$ and $h\nu_3=11.48$ eV. For the $n=1$ line calculated from Eq. (1) $h\nu_1=9.94$, again in satisfactory agreement with the experimental value of 10.17 eV for the first krypton peak. The lines at 10.81 and 11.95 eV in Kr are likely to be the second series, corresponding to $n=1$ and $n=2$ excitons generated from the lower valence band. For this series the line $n=1$ is used in order to have a rough estimate of E_G and G. The calculated values are $E_G=12.33$ and $G=1.52$ eV and they are likely to be slightly underestimated.

The experimental results for solid argon do not provide enough information to enable us to compute the band gap E_G. However, assuming that the peak at $\sim$13.8 eV corresponds to the $n=2$ exciton and taking the energy of the first doublet as 12.2 eV, a rough estimate of E_G and G can be made. It is found that $E_G\simeq 14.3$ and $G\simeq 2.1$ eV.

From the calculated values of G it is possible to determine the exciton's reduced mass μ and the radii a_n, provided that the dielectric constant is known. The dielectric constant ϵ for argon and krypton at 20°K has been extrapolated here by means of the Clausius–Mossotti relation, from the known values of the refractive index at 70–80°K and of the density as a function of temperature.[14] Because no experimental data are available for the dielectric constant of solid xenon, it has been estimated from the atomic polarizability[15] and the interatomic distance.[16]

The extrapolated dielectric constant for argon at 20°K is 1.67; from the estimated exciton binding energy $G\simeq 2.1$ eV the calculated reduced mass and first radius are $\mu\simeq 0.43$ electron masses and $a_1\simeq 3.9$ Bohr radii. In krypton $\epsilon=1.80$ and for the first series, $G=1.73$; then $\mu=0.41$ and $a_1=4.4$. In the second series, from $G=1.52$, $\mu=0.36$, and $a_1=5.0$. In xenon $\epsilon=2.23$ and $G=0.86$; then $\mu=0.31$ and $a_1=7.1$. It is interesting, at this point, to compare the $n=1$ exciton radii with the "atomic radii," here defined as the atomic separation, in the crystals, divided by two. They are 3.55, 3.78, and 4.10 Bohr radii for argon, krypton, and xenon, respectively. We see that the $n=1$ excitons are only slightly larger than the atoms but they become considerably larger when $n=2,3,\cdots$. The small peak at 9.28 eV in xenon probably does not correspond to a $n=4$ exciton because

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[11] R. S. Knox and N. Inchauspé, Phys. Rev. **116**, 1093 (1959).

[12] R. S. Knox (private communication); see also Rad. Research Suppl. (to be published).

[13] R. J. Elliott, Phys. Rev. **108**, 1384 (1957).

[14] B. F. Figgins and B. L. Smith, Phil. Mag. **5**, 186 (1960); B. L. Smith, *ibid.* **6**, 939 (1961); G. O. Jones and B. L. Smith, *ibid.* **5**, 355 (1960); E. R. Dobbs and G. O. Jones, *Reports on Progress in Physics* (The Physical Society, London, 1957), Vol. 20, p. 516.

[15] *Argon, Helium, and the Rare Gases*, edited by G. A. Cook (Interscience Publishers, Inc., New York, 1961), p. 151.

[16] A. J. Eatwell and B. L. Smith, Phil. Mag. **6**, 461 (1961).

its energy is too high and also its diameter, larger than 100 Å, would be of the same order of magnitude of the film thickness. The same argument holds for the weak line at 11.70 eV in krypton.

The experimental values of the band gap E_G and of the exciton binding energy G are in satisfactory agreement with the theoretical predictions of the reduced mass in argon (0.52).[17] The band gap expected in argon (14.3 eV), on the basis of this interpretation of our experiment, is not inconsistent with the computed gap of 12.4 eV. Knox and Bassani had indicated that this number was likely to be too low.[3]

The oscillator strengths of the different lines are proportional to n^{-3}, according to the Wannier model,[13] because the symmetries of the bands involved are undoubtedly appropriate to "allowed" transitions. From a rough analysis of the areas under the experimental peaks, the ratios of the $n=1$ and $n=2$ line areas are: 6 to 7 for argon, 4 for both series in krypton, and 9 for xenon. The predicted ratio is 8. The anomalous oscillator strength ratio in krypton and the lines in krypton and xenon, close to but apparently not belonging to the hydrogenlike series, suggests that the interpretation (b) might hold, i.e., the lines correspond to direct transitions at some other point of the Brillouin zone.[12] In solid argon the point L is a point at which the direct band gap is only slightly larger than at the point Γ.[3] Such excitons have been considered in other quite unrelated solids.[18]

In many respects, the Wannier model of the exciton seems to fit the experimental data discussed above. However, certain anomalies exist, for example, the oscillator strengths ratio observed in krypton. Theoretical studies in progress[19] on the band structure of krypton may provide the answer to this problem, but no clear-cut decision as to a particular model can be made at this time. Also, the interpretation of the higher energy structures would be, at present, rather more speculative. Other experiments on the reflectivity and on the luminescence of these materials may give the additional experimental information needed to describe more completely the energy states in the solid rare gases. The experiments are underway and will be reported on in the near future.

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[17] R. S. Knox and F. Bassani (unpublished).

[18] B. Lax, Phys. Rev. Letters 4, 511 (1960); M. Cardona and G. Harbeke, *ibid.* 8, 90 (1962).

[19] W. B. Fowler, Jr., and R. S. Knox (private communication).