Trapped Excitons in Dilute Rare-Gas Alloys*

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The ultraviolet absorption spectra of Ar, Kr, and Xe diluted in Ne, Ar, and Kr, have been measured at $6\pm 2^{\circ}$ K. The several peaks observed are ascribed to perturbed atomic resonances and transitions to Rydberg states of the impurities. An empirical relation suggests that the modes of vibration of the impurities in the host-lattices are partly responsible for the half-widths of the peaks.

I. INTRODUCTION

HE pure rare-gas solids, recently investigated in the vacuum ultraviolet, show strong absorption bands beginning at energies close to those of the lowest atomic resonances. These absorption bands have been ascribed to the creation of excitons by the absorbed photons.1

Here we report the spectra of rare-gas solids (Ne, Ar, and Kr) containing rare-gas impurities (Ar, Kr, and Xe). The present experiment has been carried out to ascertain the influence of the host matrices on the optical properties of the impurities in the hope of better understanding the fundamental properties of the pure solids. Because the impurities have essentially the same electronic configuration of the host atoms it is likely that they will not perturb the lattice very much around them. Therefore one may expect the neighborhoods of the impurities to be nearly the same as in a pure lattice. Preliminary results on one of the systems, xenon diluted in argon, have been published recently.²



FIG. 1. Typical interference effects produced when depositing rare-gas films on a cold substrate. The intensity of monochromatic (1255 Å) light reflected (at 45° angle of incidence) from a liumogen coated sapphire plate at $6\pm 2^{\circ}$ K is plotted as a function of time. The two arrows indicate the beginning and the end of the deposition of a Ne:0.7% Ar film \sim 0.23 u thick.

¹G. Baldini, Phys. Rev. 128, 1562 (1962). ²G. Baldini and R. S. Knox, Phys. Rev. Letters 11, 127, (1963).

II. EXPERIMENTAL PROCEDURE

Samples of solid rare-gas alloys were obtained by depositing the gas mixtures onto a liquid-helium-cooled substrate. Two different kinds of substrates were used, but this led to no appreciable difference in the absorption spectra. In some cases the film holder was a synthetic sapphire plate coated with an organic phosphor, liumogen,^{1,3} which converted the uv radiation into visible light which was then detected by means of a photomultiplier. The other method, useful only at wavelengths above 1050 Å, employed a LiF plate, and the transmitted uv radiation was detected by a photomultiplier coated with sodium salicylate. A good thermal contact of the sample holder with the liquid helium in the cryostat was obtained by clamping the LiF or sapphire substrates tight between thin lead or indium gaskets. The temperature of the substrates was estimated to be $6\pm 2^{\circ}$ K.

The growth of the films was monitored during the deposition of the gases by recording continuously the intensity of monochromatic light reflected by the substrate-plus-film combination. As shown in Fig. 1, before the deposition started a constant signal was recorded; then the reflected intensity dropped during the first few seconds of deposition and reached a minimum when the films were approximately a quarter wavelength thick; a maximum followed when the thickness doubled, then another minimum and so on with sinusoidal oscillations as function of thickness until the deposition was halted. The final thickness was determined by counting the number m of "wavelengths" in the recorded reflection versus time signal. More precisely

$$t = m(\lambda/2) (1/(n^2 - \sin^2\theta)^{1/2}).$$
 (1)

 θ , the angle of incidence of the monochromatic radiation, was $\sim 45^{\circ}$. The refractive indices *n* of the solid rare gases in the vacuum ultraviolet have not been measured. Here we assume that, far from the absorption region, the indices of Ar, Kr, and Xe are the same as those previously used.¹ We have estimated the neon index, ~ 1.1 , by means of the Clausius-Mossotti relation, using the static atomic polarizability and the solid density.⁴ The drop of the reflected intensity after

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³ N. Kristianpoller and D. Dutton, Appl. Opt. 3, 287 (1964). ⁴ Argon, Helium and the Rare Gases (Interscience Publishers, Inc., New York, 1961).

TABLE I. Energies and half-widths (in parentheses) of the principal absorption peaks of dilute rare-gas alloys. Energies and half-widths are in eV.

Impurity Host	Argon		Krypton		Xenon		
	³ P1	${}^{1}P_{1}$	⁸ P ₁	${}^{1}P_{1}$	³ <i>P</i> ₁	${}^{1}P_{1}$	n=2
Vacuum	11.62	11.83	10.03	10.56	8.43	9.57	
Neon	12.5 (0.2)	12.7 (0.2)	10.62 (0.15)	11.22 (0.14)	9.08 (0.135)	11.28 (0.115)	10.04 (0.095)
Argon	12.1 ^a (0.3)	12.3ª (0.4)	10.79 (0.11)	11.36 (0.10)	9.22 (0.095)	10.53 (0.085)	9.97 (0.075)
Krypton			10.17 ^a (0.15)	10.81 ^a (0.13)	9.01 (0.07)		9.76 (0.065)
Xenon					8.36ª (0.16)	9.53ª (0.2)	9.07ª (0.08)

* Pure rare-gas solids. See Ref. 1.

the deposition on LiF had begun indicates that the refractive indices of the solid rare gases, in the spectral region where they are transparent, are smaller than the index of LiF. Thicknesses ranging from a few hundred Å up to a few μ were easily obtained in from a fraction of a min up to a few min depending upon the thickness of the films. The gas flow, and therefore the rate of growth of the films, could be controlled by means of a needle valve in the deposition system.

The apparatus used in the present experiment consisted of a vacuum uv monochromator operated with a band pass of ~ 1 Å and of an open Hanovia lamp which provided the uv radiation in the spectral region investigated, i.e., between 900 and 1600 Å.¹



FIG. 2. The lower absorption spectrum is that of a Ne film $\sim 0.18\mu$ thick. The upper curve is the spectrum of a Ne:0.7% Ar film $\sim 0.23\mu$ thick. The insert shows the absorption of the film between 12 and 13 eV when the area under the dashed line is subtracted. Both films were deposited on a liumogen coated substrate at $6\pm 2^{\circ}$ K.



III. EXPERIMENTAL RESULTS

The absorption spectra of Ar, Kr, and Xe, diluted in solid rare gases of higher-band gap, are shown in Figs. 2–7. The experimental points correspond to the optical density of the films calculated at the peaks of the numerous H₂ emission lines seen at the exit slit of the vacuum monochromator. Table I lists the energies and half-widths of the absorption peaks corresponding to the lowest triplet $({}^{1}S_{0}-{}^{3}P_{1})$ and singlet $({}^{1}S_{0}-{}^{1}P_{1})$ transitions (spin-orbit doublets) of Ar, Kr, and Xe. Also shown, for Xe only, are the energies of the absorption peaks occurring between the components of the spin-orbit doublet (see Sec. IV).

The lower curve of Fig. 2 is the spectrum of an undoped Ne film while the upper curve corresponds to a Ne film containing a small concentration of Ar. The thickness of the doped film has been estimated by measuring the intensity of monochromatic light, 1255 Å in the present case, reflected by the liumogen-coated substrate while the film was being deposited on it, as shown in Fig. 1. The two arrows in the figure indicate the beginning and the end of the Ne:0.06% Ar gas deposition which required ~140 sec in order to obtain a film ~2300 Å thick. The thickness of the undoped neon film, ~1800 Å, was determined in the same way. Using the values of the above thicknesses we found that the absorption coefficient of both films was ~10⁵ cm⁻¹ at 13 eV.

In the Ne:Ar film a peak and a "hump" appear at ~ 12.7 and ~ 12.5 eV, respectively. If we assume that the absorption below the dashed line is the spectrum of pure neon, then, when subtracted from the spectrum of Ne:Ar, a doublet clearly results as shown in the insert of Fig. 2. This doublet, which is very likely due



FIG. 4. Absorption spectrum of a Kr-doped Ar film. See text for estimate of Kr concentration and film thickness. LiF substrate, $6\pm 2^{\circ}$ K.

to the Ar impurity-resonance doublet, seems to be present also in the undoped Ne film, lower curve of Fig. 2, in smaller concentration. This may indicate that the Ne gas used for this experiment contained a small ($\sim 10^{-4}$) concentration of Ar. An estimate of the Ar concentration in the doped Ne sample can be obtained from the measured thickness of the film and using the theoretical absorption cross section of the 3p-4s transition of the argon impurity.⁵ It is found that, if the doublet in the Ne: Ar film is due to the Ar 3p-4sabsorption, the Ar concentration in solid Ne was $\sim 7 \times 10^{-3}$, i.e., the concentration of the impurities increased ~ 10 times from the gas to the solid phase. This might have been expected because Ne and Ar have much different melting temperatures, and the cold substrate is more effective in freezing Ar than Ne.

Krypton diluted in neon and argon, Figs. 3 and 4, shows its resonance doublet shifted to higher energies when compared with that of the pure Kr. The peaks occur at 10.62 and 11.22 eV in neon; 10.79 and 11.36 eV in argon. The shift is smaller in neon than in argon, the linewidths larger in neon. The triplet is shifted less than the singlet. The concentration of krypton in neon can be estimated from the measured thickness of the film $\sim 3.7\mu$ and the assumption that the impurity doublet of Kr has the same absorption cross section of the argon impurity. It is found then that the krypton concentration, originally 3×10^{-4} in the gas phase, becomes $\sim 3 \times 10^{-3}$ in the solid phase, i.e., 10 times larger. The Ar: Kr film thickness has not been measured. The Kr concentration, 10^{-3} in the gas phase, is expected to increase in the solid, but less than for the previous case because the Ar and Kr melting points differ less than those of Ne and Kr. We may therefore expect that the Kr concentration in the solid Ar film is a few times 10^{-3} .

The xenon impurity shows many peaks as seen in Figs. 5–7. In neon strong Xe peaks appear at 9.08, 10.04, and 11.28 eV; weaker lines at 10.40, 10.95, and 11.48 eV. There is some evidence, as will be shown later, that the 9.08- and 11.28-eV lines are the lowest triplet and singlet of the Xe impurity, in spite of the very large spin-orbit splitting. In argon, strong Xe lines are seen^{2,6} at 9.22, 9.97, 10.53, 10.81, and 11.02 eV; weaker lines occur at 10.28, 10.39, and 10.70 eV. The Xe doublet is probably given by the 9.22- and 10.53-eV lines. In krypton the Xe triplet appears at 9.01 eV, while the singlet is almost certainly hidden in the fundamental region of the host. Another line occurs at 9.76 eV.

In order to estimate the concentration of xenon in the different hosts the absorption cross section of the pure xenon triplet at 8.36 eV has been measured and found $\sim 3 \times 10^5$ eV cm⁻¹. If we assume that the absorption cross section of the isolated impurities is about the same as that of the pure xenon, i.e., we neglect a possible difference in the local field correction, then for the 3.9- μ -thick neon film the xenon concentration should be $\sim 3.5 \times 10^{-3}$, for the 0.6 μ -thick krypton film, 11×10^{-3} . The xenon concentrations in the neon and



FIG. 5. Absorption spectrum of a Ne: $\sim 0.35\%$ Xe film $\sim 3.9\mu$ thick. LiF substrate, $6\pm 2^{\circ}$ K.

⁶ K. Dressler, J. Opt. Soc. Am. 50, 501A ((1960); J. Quant. Spectr. Radiative Transfer 2, 683 (1962). J. Y. Roncin, V. Chandrasekharan, N. Damany, and M. B. Vodar, J. Chem. Phys. 60, 1212 (1963). J. Y. Roncin, V. Chandrasekharan, and N. Damany, C. R. Acad. Sci. 258, 2513 (1964).

⁵ A. Gold, Phys. Chem. Solids 18, 218 (1961).

krypton gas mixtures were 1.7×10^{-4} and 10×10^{-4} , respectively, i.e., the impurity concentration increased in the solid 20 and 11 times, respectively. If we assume that the Xe enrichment of the Ar:0.1% Xe gas mixture used for preparing the sample of Fig. 6 is intermediate between those of Kr:Xe and Ne:Xe, we estimate a thickness of $\sim 1 \mu$ for the Xe-doped Ar film and a Xe concentration of $\sim 1.5 \times 10^{-2}$.

In all the solid rare-gas mixtures, except Ne:Ar, humps appear on the low-energy side (high-energy side in Ne:Kr) of some absorption peaks. In the Ar:Xe films, Fig. 6, the humps appear near the A_1 and B_1 lines; the A_2 and A_3 peaks are almost free from humps and their half-widths increase less than those of the A_1 and B_1 peaks when the Xe concentration is increased. The line at 9.01 eV in Kr:Xe films, Fig. 7, is accompanied by a shoulder while the 9.76-eV peak is relatively unaffected by side absorption. In Ne:Xe, Fig. 5, the 9.08- and 11.28-eV peaks have humps larger than those of the 10.04- and 10.40-eV lines. The ratio of the height of these shoulders to those of the main peaks has been found to be dependent upon the concentration of the impurity. For low concentrations the hump is rather small; at higher concentrations it becomes sometimes a broad band that overlaps the sharper triplet or singlet. It is therefore very likely that the humps are due to the presence of impurity pairs. Their energies are ~ 0.15 eV lower than those of the isolated impurities. For Kr diluted in Ne the shift is slightly greater and on the high energy side of the doublet components.



FIG. 6. Absorption spectrum of a Xe-doped Ar film. See text for estimate of Xe concentration and film thickness. LiF substrate, $6\pm 2^{\circ}$ K. See also Ref. 2.



IV. DISCUSSION

Before discussing the dilute solid rare-gas alloys it is useful to review briefly the results obtained for the pure solids.¹ The optical spectra of Ar, Kr, and Xe have strong absorption peaks at energies close to those of the lowest atomic doublets and weaker peaks apparently not related to atomic transitions. The Mott-Wannier model has been invoked to interpret both kinds of peaks, the band gaps have been estimated and important parameters of the excitons have been determined.¹ Furthermore, the calculation of the band gap and of the excitons' energies in krypton⁷ agree very well with the experimental results reviewed above. Neon, investigated here, shows broad and fairly strong absorption between 11 and 14 eV, i.e., at energies surprisingly lower than those required to excite the atom to its lowest resonance transition ~ 17 eV. This absorption bears some resemblance to the "tail" of pure argon in the long-wavelength side of the first absorption peak between 11 and 12 eV. The rather broad spectrum of Ne, contrary to the results for the other rare-gas solids, is probably related to its low melting point. The experimental temperature $6 \pm 2^{\circ}$ K, is relatively high for the solid, and therefore we can expect many imperfections to exist, causing broad absorption at long wavelengths instead of an otherwise sharper spectrum at showter wavelengths.

The optical absorption spectra of dilute rare-gas alloys have many of the features observed in the pure solids. These are essentially: (a) the presence of strong peaks apparently derived from atomic doublets, and (b) the appearance of weaker lines which seem to have

⁷ W. B. Fowler, Phys. Rev. 132, 1591 (1963).

different origin. The doublets, which with very little doubt correspond to the lowest resonance triplet and singlet transitions of the impurities, are all blueshifted as seen in Table I. Qualitative agreement exists between the experimental and theoretical⁵ data for the Ar impurities in Ne. The slightly larger "blue" shift of the singlet is also predicted.

The krypton-doped rare gases show only the spinorbit doublet of the impurity. The presence of the fundamental edge of both the Ne and Ar hosts close to the doublet hides possible impurity transitions occurring at higher energies.

The xenon impurities, on the other hand, show other lines besides those of the doublet. The Ar: Xe system has been discussed previously² and here we will just summarize the analysis of its spectrum. The lines labelled A_1 and B_1 in Fig. 6 are the two components of the Xe spin-orbit doublet. The lines A_2 , A_3 , and A_4 are ascribed to hydrogen-like excitations of the Xe impurity in its triplet states. The A_1 line is the lowest triplet, but it cannot be made to fit the hydrogen-like series for reasons given before.² When the impurity is diluted in krypton only two lines can be observed (Fig. 7). The one at lower energy is apparently the lowest triplet and the other is very likely the n=2line of the triplet series. The presence of the krypton absorption edge at ~ 10 eV hides other lines of the series which could enable us to determine the values of important quantities as the mass of an electron in the conduction band of krypton.

When xenon is diluted in neon, Fig. 5, the lowest triplet of Xe is certainly the line at 9.08 eV. In order to locate the lowest singlet we make the following observations: When the Xe concentration increases, the lines at 10.04 and 11.40 eV have a behavior similar to that of the A_2 and A_3 lines in Ar:Xe, i.e., they stay relatively sharp while the peak at 11.28 eV displays a hump similar to that near the 9.08 eV line. The 11.28eV line is probably the lowest Xe singlet although it seems a little difficult to justify the large "spin-orbit" separation, 2.20 eV which compares with 1.31 eV for Ar: Xe and 1.17 eV in vacuum. Nevertheless, the similarity with the Ar:Xe spectrum suggests that the 10.04-eV line is the n=2 triplet and the 10.40-eV peak includes the remainder of the triplet series, ie., the $n=3, 4, \cdots$ lines. Using the energies of the two peaks at 10.04 and 10.40 eV we can estimate^{1,2} the lowest energy required to ionize the Xe impurity in solid neon, ~ 10.7 eV, and the effective mass of an electron in the conduction band of neon, 0.3 electron mass units. Another interpretation which avoids the introduction of an extremely large spin-orbit splitting is the following⁸: The n=1 states from the higher ("singlet") series and the n=2 states from the lower ("triplet") series might both fall at about 10.2 eV in zero order, but configuration interaction mixes them and splits

them apart, causing levels at 10.04 and 10.40 eV. It does not appear possible to decide between these alternatives without detailed calculations.

The study of the half-widths of the trapped excitons shows a suggestive dependence upon both the mass of the impurities and the mass of the host atoms. We find that the half-widths W of the n=1 lines can be described by the empirical formula

$$W_{ih} = A M_h^{-1/2} M_i^{-1/4}, \qquad (2)$$

where the subscripts i and h refer to the impurity and host atoms, respectively. For the triplets ${}^{3}A = 2.09 \pm 0.06$ eV (atomic mass units),^{3/4} and for the singlets ${}^{1}A$ =1.84 \pm 0.07 eV (atomic mass units)^{3/4}. The n=2triplets of Xe satisfy the following relation

$$W_{ih} = BM_{h}^{-1/4},$$
 (3)

with $B=0.225\pm0.008$ eV (amu)^{1/4}. We note here that the half-widths are measured to within ± 0.005 eV which is an uncertainty of $\pm 5\%$ for the average halfwidth. If these empirical relations are not fortuitous, then we can make the following remarks:

(a) The presence of the mass of the impurities in the formula suggests that the dynamics of the impurities contributes to the half-widths.

(b) The n=1 and n=2 triplets obey different formulas and therefore we may assume that there is an intrinsic difference between the lowest and the higher excitons.

Dawber and Elliott⁹ have shown that the rms displacement of an impurity at low temperature can be expressed in terms of the rms displacement of the atoms of the host crystal and of the masses of the impurity atoms:

$$u_i = u_h M_h^{1/4} M_i^{-1/4}, \qquad (4)$$

where u_i and u_h are the rms displacements. From an expression of u_h , also given in Ref. 9, we find that at low temperature

$$u_h \propto \Theta_D^{-1/2} M_h^{-1/2},$$
 (5)

and therefore, substituting from (5) we can write (4) as

$$u_i \simeq \Theta_D^{-1/2} M_h^{-1/4} M_i^{-1/4}, \qquad (6)$$

where Θ_D is the Debye temperature of the host. If we assume that in the rare gases $\Theta_D^{-1/2}$ is approximately constant (its values are actually 0.125, 0.112, and 0.126 for Ne, Ar, and Kr, respectively), then (6) becomes

$$u_i \propto M_h^{-1/4} M_i^{-1/4}.$$
 (7)

Rabin and Reich¹⁰ have found that the half-width of the F band in LiF is proportional to $M^{-1/4}$, where M

⁸ R. S. Knox (private communication).

⁹ P. G. Dawber and R. J. Elliott, Proc. Roy. Soc. (London) A273, 222 (1963). [Evidently a misprint occurs in Eq. (5.6) in this paper. Our Eq. (4) is the correct version.] ¹⁰ H. Rabin and M. Reich, Bull. Am. Phys. Soc. 9, 89 (1964).

is the mass of the Li ions surrounding the center. We then assume here that the half-widths of the n=1trapped excitons in the rare-gas solids are determined by the product of a "local mode" factor proportional to the rms displacement of the impurity, and by a "neighbor" factor which is determined essentially by the neighbors of the impurity according to the following relation:

$$W_{ih} \propto M_h^{-1/4} (\text{neighbors}) \times M_h^{-1/4} M_i^{-1/4} (\text{local}).$$
 (8)

This is just like Eq. (2), the empirical relation for the n=1 doublets. A dependence of the linewidth upon the mass of the impurity has been observed also in solid Ar containing hydrogen and deuterium impurities¹¹ and in the U band of alkali halides containing $H^$ or D⁻ ions.¹² The n=2 states obey Eq. (3) rather than (2); we do not know whether or not the mass of the

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impurity enters Eq. (3) because these lines have been observed only in the Xe-doped rare-gas solids. (The Kr-doped samples show only the n=1 doublet which lies close to the absorption edges of the neon and argon hosts.) Because of the difference between Eq. (2) and (3) it appears that the interaction of the lattice vibrations with the n=1 and n=2 excitons is different. This assumption is supported also by the fact that the wave functions of the n=1 states are confined to within the unit cell contrary to the n=2 states which extend over a larger volume of the crystal.^{1,2}

Experiments on photoconductivity and luminescence, now in progress, are expected to yield more detailed information on the electronic and vibrational states of the rare-gas solids.

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Resistivity of Solid and Liquid Sodium*

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This paper reports a theoretical study of the resistivity of solid and liquid sodium. It utilizes inelastic neutron scattering data to obtain the required information about the dynamics of the ions. The electronphonon interaction is characterized by phase-shifts η_l , two of which are used as adjustable parameters. Although the calculation is believed to incorporate accurately many-body effects, umklapp processes, timedependent effects, etc. agreement with experiment is disappointing. The calculated resistivity exceeds the experimentally measured values by a factor of the order of 2 at low temperatures, and above the melting point there are again discrepancies of this order. No convincing explanation of these disagreements has been found.

I. INTRODUCTION

NE of the basic tasks of solid-state theory has been to account for the electrical resistivity of simple monovalent metals. The qualitative features of the resistivity of the solid phase, both at very low and at higher temperatures were first theoretically accounted for by Bloch.¹ The next most important landmark was a calculation by Bardeen² who, starting from first principles, was able to give a good quantitative description of the resistivity of sodium and other monovalent solid metals in the high-temperature region. Since then many other calculations on solid metals have been carried out, notably the work of Ziman³ and Bailyn.⁴

A qualitative theory for liquid metals has also been developed by Ziman.⁵

The present work was motivated by the realization that for both solid and liquid sodium experimental data and theoretical methods were available which should enable one to eliminate, within a few percent, all the uncertainties which were known to have been present in past calculations. These included uncertainties about:

(1) The dynamics of the ions.

(2) The ion-electron interaction, including manybody effects.

- (3) The validity of the Boltzmann equation.
- (4) The handling of umklapp processes.

For these reasons, good agreement over a wide temperature range was expected.

 ¹¹ G. Baldini, Phys. Rev. 136, A248 (1964).
 ¹² G. Baldini (to be published).

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¹ F. Bloch, Z. Physik, 52, 555 (1928).
² J. Bardeen, Phys. Rev. 52, 688 (1937).
³ J. Ziman, Proc. Roy. Soc. (London) A226, 436 (1954).

⁴ M. Bailyn, Phys. Rev. 120, 381 (1960).

⁵ J. Ziman, Phil. Mag. 6, 1013 (1961).