purities, an effect which may be due to the differences between the level structures of Mn and Gd, and to the different positions of their levels with respect to the Fermi energy. Crystal-field effects, which so far have not been directly observed, may also contribute to the difference in behavior of the two ions. The difference in broadening by rare-earth impurities in the cases of Mn and Gd can then be understood, since Gd reacts only to the magnetic disturbances of the other rare earths, whereas Mn is also broadened by the nonmagnetic disturbances set up by these impurities.

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$1s$–$2p$ Transition of H and D in Solid Argon*

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The $1s$–$2p$ transition of hydrogen and deuterium atoms diluted in solid inert gases has been observed and its energy and half-width measured. In argon, absorption occurs at the energies of 10.55 and 10.565 eV and the half-widths are 0.27 and 0.23 eV, respectively, for H and D. An analysis of these results leads to an estimate of the frequency of a localized vibrational mode associated with the H and D impurities.

I. INTRODUCTION

Among the several methods used to investigate the properties of a solid is the introduction of impurities in the otherwise pure matrix. By studying the properties of the impurities as perturbed by the host lattice, it is possible to gain some knowledge about the electronic and vibrational structure of the lattice. Hydrogen, and its isotope deuterium, may be considered the simplest impurities and their unperturbed electronic structures are essentially known exactly; therefore they are convenient probes when introduced in the appropriate solids. If the optical absorption of these impurities is to be investigated there are only a few solids that can be used as hosts, the reason being that the resonance transitions of H and D occur above 10 eV, i.e., in the Lyman region of the vacuum ultraviolet where almost all solids absorb strongly.

The present paper reports the study of Ar and Ne films containing H or D as impurities.[1] The experiments show isotope effects, and one interpretation of the results leads to a determination of the frequency of a localized mode interacting with the $1s-2p$ transition of the H or D impurity centers.

II. EXPERIMENTAL

Hydrogen and deuterium atomic impurities have been produced by applying radio-frequency voltage at $\simeq$30 Mc/sec to the gases in their molecular form. The rf was applied either to the H_2 (or D_2) gas alone or to Ar (or Ne) containing a small fraction of H_2 (or D_2). In the first case, two separate deposition systems, one for Ar (or Ne) and the other for H, were employed, each of them ending in a capillary pointing toward a cooled substrate. When the rf was applied to a pyrex capillary with H_2 or D_2 flowing, it produced a red glow very rich in Balmer lines and only a very weak molecular spectrum, thereby indicating the predominance of atoms over molecules. The alternate method was to apply the rf to a mixture of Ar (Ne) and H (D) while it flowed toward the LiF film holder. The ratio of H to Ar was of the order of 2%, and even in this case the Balmer lines could be easily seen among the Ar lines.

The LiF substrate was at a temperature of 5±1°K at the end of a liquid helium-cooled cryostat, as described along with the rest of the experimental apparatus in a previous paper.[2]

III. EXPERIMENTAL RESULTS

The spectra of H- or D-doped argon films investigated between 1050 and 2200 Å exhibit absorption in the Lyman α spectral region as shown in Fig. 1. The open-circle spectra correspond to films produced by applying the rf to H or D only, while in the case of full-circle spectra, Ar:H (D) mixtures were treated with rf. The H and D bands occur at 10.56±0.01 eV, with the D band shifted by $\approx$0.015 eV from the H band toward higher energies. The energy of the transition for the trapped atoms is thus 0.36 eV greater than for the free atoms. The half-widths of the absorption bands are

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[*] Research supported in part by the U. S. Air Force Office of Scientific Research.

[1] For preliminary results, see G. Baldini, Bull. Am. Phys. Soc. 9, 217 (1964).

[2] G. Baldini, Phys. Rev. 128, 1562 (1962).

0.27±0.01 and 0.23±0.01 eV for H and D, respectively. The bands, at least above their half-maxima, appear to be symmetric. No significant difference has been found between spectra obtained from samples prepared by the two methods of introduction of impurities.

A phosphorescence was always detected after the deposition had been terminated. A sodium-salicylate-coated photomultiplier employed for the absorption measurements could detect light, from the H- or D-doped samples, which decayed with a time constant of a few minutes. The total amount of afterglow seemed to be proportional to the amount of gas that had been treated with the rf, and it is likely therefore that the phosphorescence was produced by the recombination of ions and electrons and perhaps also by H or D atoms forming molecules.

The absorption edge beginning at ~11 eV is probably due to the Ar host,[2] although some contribution may also come from higher excited states of atomic hydrogen or from the resonance transitions of molecular hydrogen.[3]

Neon films doped with D show a broad and weak absorption between 10 and 11 eV (Fig. 2), which could well be due to the 1*s*–2*p* transition of the impurity. However, because of the rather high zero-point energy of neon, it is possible that recombination of D atoms can take place faster than in argon, consequently reducing the concentration of isolated atoms and creating molecular centers. The edge at ~11 eV, where hydrogen molecules absorb,[3] suggests that in neon, it might be difficult to keep the D atoms isolated from each other.

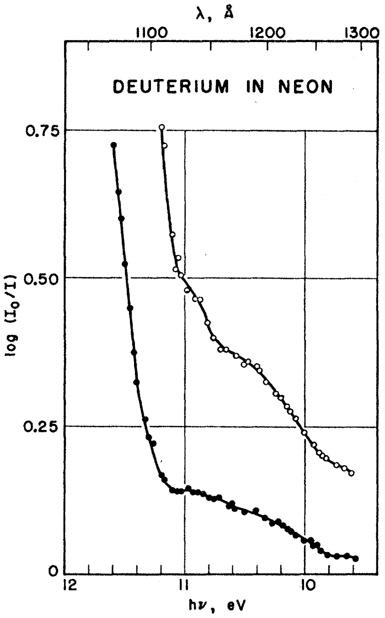

FIG. 2. Absorption spectra of neon containing deuterium at 5±1°K. Open and filled circles have the same meaning as in Fig. 1.

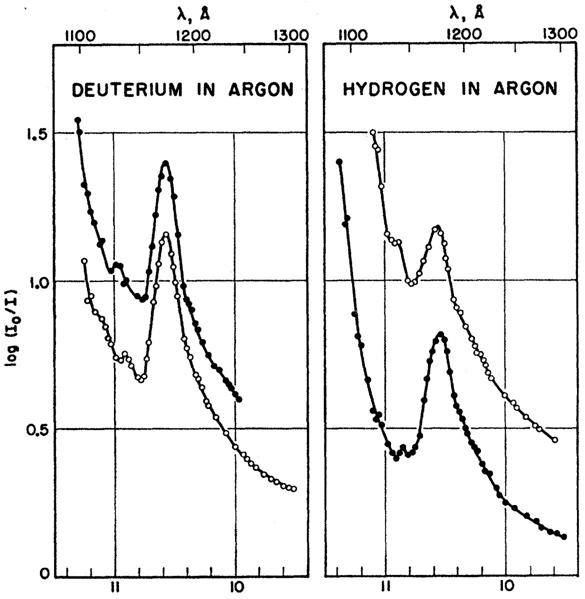

FIG. 1. Absorption spectra of argon containing atomic deuterium or hydrogen impurities measured at 5±1°K. ●—samples produced by applying the radio frequency to gaseous mixtures of Ar:H_2 (or D_2). ○—spectra have been obtained by applying the radio frequency only to the H_2 or D_2 gases.

The concentration of H or D in the argon films has not been measured, but we believe that because hydrogen freezes only at very low temperatures it may be a few times smaller than the 2% quoted above for the gas ratio.

IV. DISCUSSION

The absorption at 10.56±0.01 shown by the Ar films is very likely caused by the 1*s*–2*p* transition of H or D atoms trapped in the argon lattice. We believe that the absorption is due to atomic H or D and not molecule or Ar ions for the following reasons:

The absorption of H_2 or D_2 occurs at energies greater than 11 eV, and it is a quasicontinuum.[3]

Samples of Ar not previously doped with H or D, but treated with the radio-frequency, have spectra similar to that of pure argon,[2] with the exception of two small peaks about two orders-of-magnitude weaker than the H or D bands in the doped films. The two peaks occur at approximately 10.55 and 10.85 eV, the first being slightly weaker than the second. A tentative interpretation is that they belong to excitons created near Ar^+ ions which can be certainly produced in the rf discharge and injected into the films. It is likely that the weak peak observed at energies between 10.85 and 10.96 eV in doped Ar (Fig. 1) corresponds to one of these "trapped excitons," although transitions of the H or D impurities to higher excited states cannot be ruled out.

The lattice surrounding the H or D atoms apparently has the following effects on their properties:

(i) The energy of the 1*s*–2*p* transition for the trapped

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[3] G. H. Dieke and J. J. Hopfield, Phys. Rev. 30, 400 (1927).

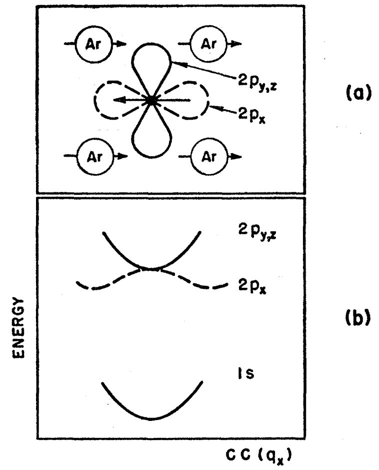

FIG. 3. (a) Localized vibrational mode of hydrogen in a substitutional Ar lattice site. The impurity is shown in its $2p$ states. (b) Energy versus *CC* for both ground and excited state of hydrogen.

H or D atoms is greater than that of the free atoms by about 0.36 eV. (ii) Because of atomic vibration, the half-widths of the H and D bands are much larger than the natural ones. (iii) Isotope effects occur. The H absorption energies and band half-widths are different from those of D.[4]

The "blue shift" of the $1s$–$2p$ transition in the solid is consistent with the results for other impurities, e.g., Xe and Kr diluted in argon,[5,6] and can be justified as follows. In the $1s$ ground state of hydrogen the Coulomb interaction between electron and proton is essentially that of the free atom because the $1s$ wave function is small compared with the size of an argon atom (or vacancy) and it is assumed here that the impurities are in substitutional sites. For higher excited states the p wave functions of hydrogen overlap the surrounding atoms, and the electron is partially screened from the nucleus. The resonance transition energies of H or D can then be written as

$$h\nu_n = [1-(\alpha/n^2)]\ \mathrm{Ry},$$

where α, which is unity for the free atoms, is expected to go from nearly 1 for $n=2$ to $m_e^*/\epsilon_n^2 = 0.16$ for large n's, and m_e^* is the effective mass of an electron in the conduction band of argon and ϵ_n an effective dielectric constant[5] for the nth orbit.

Because the energy and half-width of the $1s$–$2p$ absorption depend upon the isotope employed, we must assume that highly localized vibrational modes are responsible for the isotope effects. Furthermore, the breathing mode of the nearest neighbors cannot account for the observed effects.

A calculation of the $1s$–$2p$ and $1s$–$2s$ transition energies of H in Ar has been carried out by Keil and Gold.[7] They are able to reproduce our excitation energy by choosing a nearest-neighbor separation of 7.0 Bohr radii in an assumed substitutional configuration. (The normal separation in the perfect lattice is $7.1a_0$.)

The broadening of the lines arises from the interaction of the electronic states with the lattice vibrations, and it is customary to describe this interaction by means of a configuration coordinate diagram.[8] For simplicity, only one configuration coordinate q is used, and the potential energy for the ground state is assumed to be quadratic in q:

$$E_g = \tfrac{1}{2}K_g q^2,$$

where K_g is an effective force constant which represents the interaction of the impurities with the argon lattice for small displacement around their equilibrium positions.

It is also known that impurities which are lighter than the host lattice generally introduce strongly localized vibrational modes,[9] and then we assume that q, the configuration coordinate (*CC*), refers only to the motion of H (or D) itself. (This being the case, one *CC* is not really sufficient, because the corresponding classical vibrational mode is threefold degenerate. Our q is taken to be one of these three coordinates.) The ground vibrational state is nondegenerate (totally symmetric), and we need not consider explicitly excitations into the first (triply degenerate) excited vibrational state because the experiment under discussion has been performed at low temperature.

Figure 3(a) represents the H impurity in a substitutional Ar site, and the arrows refer to the q_x normal mode of vibration for the system. Figure 3(b) illustrates possible energy versus *CC* curves for both the $1s$ ground state and $2p$ excited states of H. It should be noted that the energy of the system as a function of q_x must be symmetric in q_x, so that the excited state *CC*'s have vanishing slope at $q_x=0$. We postulate that the p state lying parallel to q_x, called $2p_x$, has a *CC* as shown in Fig. 3(b); it can have minima because the lobes of the $2p_x$ function are moving into the relatively empty octahedral interstitial position of the lattice. The $2p_y$ and $2p_z$ states must, on the other hand, bump into the nearest neighboring argon atoms. The energy versus *CC* for the various $2p$ states in the vicinity of $q_x=0$ is then approximated by two segments of constant slope, and the configuration coordinate theory now leads to the following predictions[10]:

(a) The absorption half-widths are inversely proportional to the fourth roots of the reduced masses of the

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[4] Isotope effects have been recently observed also in the F center of LiF [H. Rabin and M. Reich, Bull. Am. Phys. Soc. **9**, 89 (1964)], and in KCl:OH and KCl:OD [F. Fischer, Solid State Commun. **2**, 51 (1964)].

[5] G. Baldini and R. S. Knox, Phys. Rev. Letters **11**, 127 (1963).

[6] G. Baldini (to be published).

[7] T. H. Keil and A. Gold, Bull. Am. Phys. Soc. **9**, 217 (1964), and following paper, Phys. Rev. **136**, A252 (1964).

[8] See, for example, D. L. Dexter, Nuovo Cimento Suppl. **10**, 245 (1958).

[9] See, for example, R. F. Wallis and A. A. Maradudin, Progr. Theoret. Phys. (Kyoto) **24**, 1055 (1960).

[10] C. C. Klick and J. H. Schulman, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1957), Vol. 5.

oscillating systems (the two hydrogen isotopes in the present case):

$$W_i = \text{const} \times \mu_i^{-1/4}.$$

(b) The angular frequency of the localized modes interacting with the electronic states are inversely proportional to the square root of the reduced mass of the two isotopes:

$$\omega_i = \text{const} \times \mu_i^{-1/2}.$$

(c) From (b) we expect the energies of the lowest vibrational states, zero-point levels, to be different and therefore also the 1s–2p transition energies E_i at the center of the line will be different:

$$E_j - E_i = \tfrac{3}{2}\hbar\omega_i - \tfrac{3}{2}\hbar\omega_j = \tfrac{3}{2}\hbar\omega_i[1 - (\mu_i/\mu_j)^{1/2}].$$

For $\mu_D/\mu_H = 2$, (a) gives a theoretical ratio of 1.19 for the half-widths of the H and D bands, in good agreement with the measured ratio $W_H/W_D = 1.17 \pm 0.02$. The effective ω lies in the far infrared, and since our system is neutral, a very small oscillator strength is expected. In agreement with (c), the energy of the peak of the D band is higher than that of the H band. From the measured difference at the peaks, $E_D - E_H \simeq 0.015 \pm 0.003$ eV, we find $\omega_H = 2\pi(8.2 \pm 1.6) \times 10^{12}$ and $\omega_D = 2\pi(5.8 \pm 1.2) \times 10^{12}$ sec^{-1}. The Debye frequency for Ar[11] is $\omega_m = 2\pi \times 1.67 \times 10^{12}$ sec^{-1}.

The energy of the ground state as a function of q is obtained by calculating the force constant

$$K_g = \omega_H^2 \mu_H = \omega_D^2 \mu_D = 0.3 \pm 0.1 \text{ eV Å}^{-2},$$

and it is shown in Fig. 4. The value of K_g thus obtained is of the same order of magnitude of that estimated from a Lennard-Jones potential for an Ar atom in the Ar matrix ($K_{Ar} \simeq 0.3$ eV/Å^2).[11] The vibration amplitude u, measured between the points where the probability is one half of the probability at $q = 0$ is given by

$$u_i^2 = 8(\ln 2)\hbar(\mu_i\omega_i)^{-1} = 8 \ln 2\langle x^2 \rangle.$$

We then find

$$\langle x_H^2 \rangle^{1/2} = 0.35 \pm 0.04,$$
$$\langle x_D^2 \rangle^{1/2} = 0.29 \pm 0.03 \text{ Å},$$

which are to be compared with the values of 0.46 and 0.39 Å that we derive from the predictions of Dawber and Elliott on the basis of the Debye model and no change in the force constant.[12]

According to the *CC* model, the linewidth of the transition can be expressed, as shown in Fig. 4, in the following form:

$$W \simeq u(dE_e/dq)_{q=0},$$

where E_e is the energy for the excited configuration. From the experimental value of W and the calculated amplitude u for H or D we find

$$(dE_e/dq)_{q=0} \simeq 0.33 \text{ eV/Å}.$$

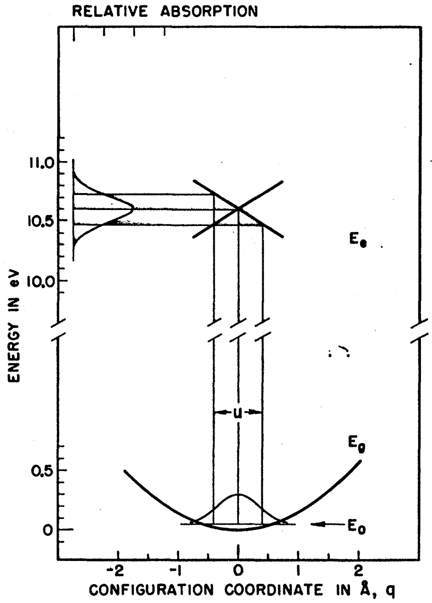

FIG. 4. Energy versus configuration coordinate for the 1s and 2p states of H and D impurities in Ar. E_g and E_e are, respectively, the ground- and excited-state energies versus the configuration coordinate q; E_0 is the zero-point energy of the centers in their ground states. For purposes of clarity, only the H transition is shown here. D has lower zero-point energy and smaller half-width.

Both the H and D bands are not symmetric below their half-widths because a "tail" or broad band appears on their low-energy side. The presence of different hydrogen trapping sites in the fcc lattice of argon, as electron-spin-resonance experiments seem to suggest,[13] might explain the "tail." Also if the concentration of interacting impurities is large, we might expect a "tail." This second hypothesis could in principle be checked by reducing the concentration of H or D in the samples; however, the thicker Ar films needed in this case have very low transmission in the region of the 1s–2p transition, and accurate measurements do not seem possible.

In conclusion, the study of the resonance transitions of H and D in solid argon shows that their energies and line widths depend upon the isotope employed. In particular, the half-widths seem to be inversely proportional to the fourth root of the masses of the two isotopes. Experiments now in progress here show that similar effects occur also in alkali halide crystals containing H$^-$ or D$^-$ ions (*U* centers).

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[12] P. G. Dawber and R. J. Elliott, Proc. Roy. Soc. (London) **A273**, 222 (1963).

[13] S. N. Foner, E. L. Cochran, V. A. Bowers, and C. K. Jen, J. Chem. Phys. **32**, 963 (1960).