in (7) and (8) seem to agree with Hempstead's[5] ESR of Mn^{2+} in $CaWO_4$. Such a comparison, however, should not be taken seriously, and for a better understanding of the results in (7) and (8) further experimental work on Mo^{5+} and its isoelectronic ions such as Cr^{5+} and W^{5+} should be undertaken.

Regarding the preferential reduction of the substitutional Mo^{6+} impurity in $CaWO_4$, we believe that oxygen vacancies created during vacuum reduction are trapped in oxygen sites surrounding the substitutional Mo^{6+} ions permitting them to acquire an additional electron. This is plausible if one considers the lower binding energy of oxygen to Mo^{6+} compared to W^{6+}.

The observed increase of the Mo^{5+} signals with increased Nd content and the reduction of this effect with Na compensation is not yet understood. Further studies to resolve this problem are under way.

ACKNOWLEDGMENTS

It is a pleasure to acknowledge the interest and stimulating discussions by Dr. D. C. Cronemeyer and Dr. R. K. Mueller and also by Professor C. Kikuchi. Technical aid by E. Spencer, M. W. Beaubien, and S. Catalano is greatly appreciated.

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[5] C. F. Hempstead and K. D. Bowers, Phys. Rev. 118, 131 (1960).

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Optical Absorption Spectra of Alkali Atoms in Rare-Gas Matrices*†

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This paper reports studies of the optical absorption spectra of alkali-doped rare-gas crystals. The samples were formed by deposition from a mixed beam of the two constituents onto a cold plate. Eight combinations of Na, K, Rb, and Cs in Ar, Kr, and Xe were studied. In each case the spectrum consisted of two triplets, one of which was centered at approximately the free-atom value and one of which was shifted to the blue by roughly 1400–1800 cm^{-1}. The relative intensity of the two triplets could be changed by varying the deposition conditions; the unshifted triplet became dominant when the sample was deposited directly on a helium-filled Pyrex tube. The interval between the three components of the unshifted triplet was roughly the same for all combinations of alkali-metal atom and rare-gas matrix. In order to understand the nature of the site, a configuration coordinate scheme was invoked to deal with the energy shifts and the linewidths, and a crystalline-field approach was employed to explain the level splittings. The first analysis indicates that the sites are not substitutional and the second that the splitting can be understood in terms of a lattice distortion which is the same in all cases.

INTRODUCTION

THERE are a number of radioactive alkali-metal atoms which one would like to orient in order to study the emission of the beta and gamma radiation. The only available method through which they can be oriented is by gas-cell optical pumping. The optical-pumping techniques have a number of difficulties and have not been used successfully to study the radiation from oriented nuclei. The number of atoms which can be oriented is small, the nuclei become polarized rather than aligned, and there tend to be more atoms on and in the wall than in the volume of the cell. The research reported in this paper was initiated to see if one could trap an alkali-metal atom in a frozen rare-gas matrix and then orient it by the absorption of circularly polarized photons. Alternately, one could use a high magnetic field and dynamic orientation methods to orient the alkali atom.The success of either scheme of orientation depends in detail upon the distortion of the atomic energy levels by the lattice, the quenching of the orbital angular momentum, and the relaxation times. In addition to a possible application in nuclear orientation experiments, such an impurity center is of interest for the light it sheds on certain problems in solid-state physics. This paper reports the initial studies of the optical absorption spectrum of such centers.

In these investigations we have proceeded along lines quite similar to those in *F*-center research. We shall use the term *A* center to refer to these atomic centers. In our case, samples consisting of many small crystals were grown by deposition from a mixed beam of the two constituents. The absorption spectra were observed for eight combinations of sodium, potassium, rubidium, and cesium in argon, kryton, and xenon in the region from 4000 to 10 000 Å. The spectra were measured for various deposition conditions and then a configuration coordinate model and a crystalline-field model were em-

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ployed to interpret and understand the major features of the spectra.[1,2]

APPARATUS

In preparing the samples, we adopted the methods developed for free-radical stabilization,[3,4] with minor modifications necessitated by the use of a constituent which is solid at ordinary temperatures. Generally, samples have been prepared by directing two independently controlled gas beams at a cold collecting plate, the concentrations being varied by changing the flow rates. We chose to dope the inert gases with alkalis by flowing the gas through an oven containing the alkali metal, controlling the alkali concentration by varying the temperature (alkali vapor pressure), and keeping the pressure of the inert gas roughly constant, usually at 1–3 mm Hg. This method insures the homogeneity of the mixture being condensed.

The oven was constructed in the familiar molecular-beam fashion by drilling a tapered reservoir in a block of stainless steel and closing it with a taper pin. The gas was admitted through a thin-walled stainless tube heliarc welded into the oven, and the mixed beam left the oven through a 0.032-in.-diam, $\frac{3}{8}$-in.-long hole. Commercial grade argon was purified by passage through a charcoal trap cooled with a dry-ice–acetone mixture; research grade gases, xenon and krypton, were used without further ado. The gas pressure in the oven was monitored with an oil manometer and controlled with a Nier leak.

Figure 1 shows a cross section of the sample deposition system. The samples were collected from the beam on a square glass tube filled with liquid helium. This tube was attached to the metal Dewar by a Housekeeper seal[5] which cycled to room temperature repeatedly without failure. In order to obtain an optical path free from bubbles, the liquid helium was pumped below the lambda point. In early experiments, the samples were deposited on a sapphire plate, which was pressed against a copper block on the bottom of the Dewar by a spring-loaded copper plate. As explained later, the spectra obtained in this manner were more complex than those obtained using the glass tube; for this reason the sapphire was abandoned.

The Dewar was constructed with a rotating vacuum seal in order to make the optical observations more convenient. The system was pumped from directly below the Dewar with a 300-liter/sec oil diffusion pump backed by a 6-liter/sec forepump. The pressure of the system was roughly 10^{-7} mm Hg and rose to roughly 1 μ during deposition of the sample.

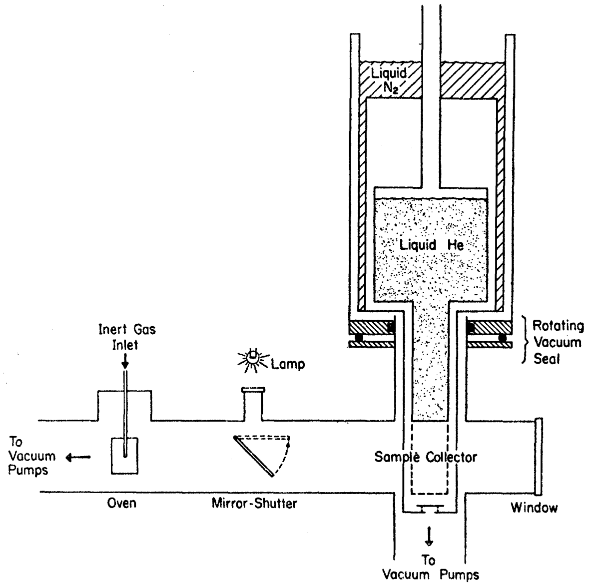

FIG. 1. Cross section of the basic apparatus for collecting and preserving the samples.

Figure 2 shows the optical system used for recording the absorption spectra. For optimum optical efficiency, ribbon-filament microscope lamps (6 V, 18 A) were used to provide the continuous spectrum from 4000 to 10 000 Å. These lamps were powered from a transistor regulated dc supply to insure constant color temperature throughout a run.

The spectral measurements were made with a Jarrell-Ash Type-8200 0.5-m Ebert scanning spectrometer. This instrument was supplied modified to accept two gratings: one to cover the range 2000–8000 Å in first order and blazed for maximum intensity at 5000 Å and the other for the range 4000–16 000 Å and blazed for 10 000 Å. The latter was used for all runs except a few of sodium in argon.

The transmission was monitored with a 2-in. end-window photomultiplier in a Jarrell-Ash housing which

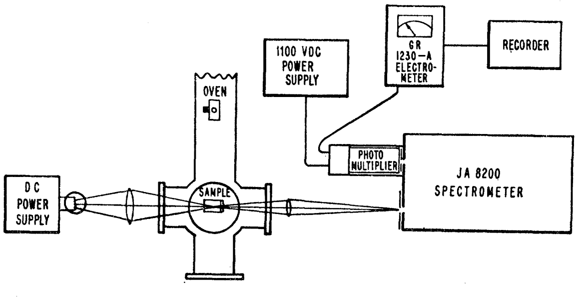

FIG. 2. The optical system used to measure the absorption spectrum.

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[1] For a general review of the theory of optical properties of imperfections in nonmetals see the article by D. L. Dexter, in *Solid State Physics,* edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1958), Vol. 6, pp. 353–411.

[2] For a general review of the properties of rare gases in the solid state see Gerald L. Pollack, Rev. Mod. Phys. **36**, 748 (1964).

[3] E. D. Becker and G. C. Pimentel, J. Chem. Phys. **25**, 224 (1956).

[4] A. M. Bass and H. P. Broida, *Formation and Trapping of Free Radicals* (Academic Press Inc., New York and London, 1960).

[5] Purchased from Larson Electronic Glass Company, Redwood City, California.

fitted over the exit slit of the spectrometer. Two photomultipliers were used: a quartz window, blue sensitive DuMont K1306 and an infrared sensitive DuMont 6911. The infrared tube had a particularly low dark current and was used for most of the measurements. The anode end was at ground potential, and the load resistance was the internal input resistor of a General Radio Type 1230-A dc amplifier and Electrometer which served as the output indicator and recorder driver.

EXPERIMENTAL PROCEDURE

Before each run, the spectrum of the tungsten lamp was recorded. The lamp was operated about 20% below its rated current to insure constant output over long periods and to give long life. Samples of undoped argon showed no spurious absorption due to interference or other effects in the sample.

Under the conditions of this experiment, the evaporation rates of the alkalis were about 100 times their flux out of the oven; so that for the purpose of computing the sample concentration, we assume the alkali concentration to be that in equilibrium at the oven temperature. The sample concentration deduced from the ratio of the alkali partial pressure at the oven temperature to the gas pressure in the oven was usually 1 to 1000. Differences in the accommodation coefficients for condensation would change the actual concentration in the solid; we shall by necessity refer to the gas concentration. With flow rates of 10–100-μliter/sec, samples of sufficient optical density were formed in one-half to a few hours.

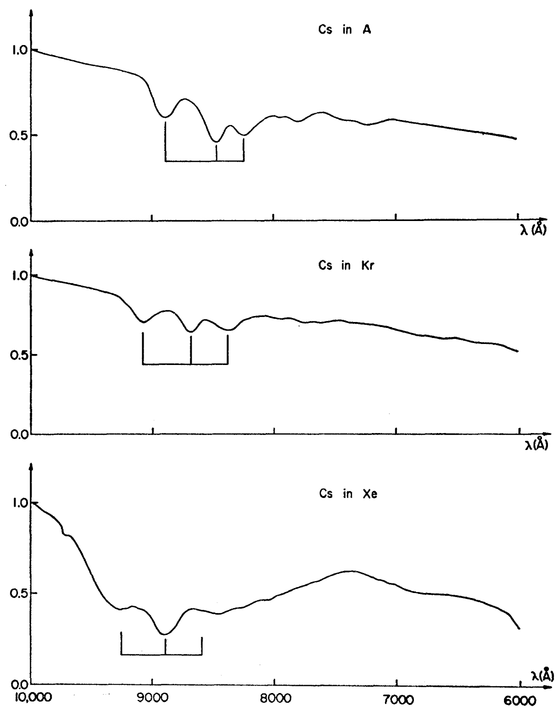

FIG. 3. The spectral transmission of the cesium A centers. These spectra were plotted out by taking the ratio between the photomultiplier current at given wavelengths for the tungsten lamp with and without the sample.

Since we did not use a dual-beam comparison spectrometer, the recorded output was the transmitted intensity and not the transmission coefficient. Broad absorption lines on sloped sections of the response show an apparent shift in the wavelength of maximum absorption. By a straightforward geometrical comparison with the initial tungsten spectrum, the apparent absorption peaks were corrected without resorting to a point-by-point plot of the spectrum. Point-by-point computations at 15-Å intervals were employed to plot the cesium spectra in terms of the transmission coefficient. The resulting spectra are shown in Fig. 3. The results obtained from the two methods agreed within the quoted error in all cases and on the average to less than half that error. The spectrometer errors are estimated to be ess than 2 Å and are included in the quoted errors.

RESULTS

We measured the absorption spectrum of eight combinations of alkalis in inert-gas matrices in the 4000–10 000-Å region. In all the cases studied, the absorption consisted of one or more strong triplets. In the case of cesium in xenon, the position of one component of the triplet was ambiguous because of the presence of weaker subsidiary lines (see Fig. 3); in all other cases, the spectra were well-defined.

As mentioned above, two different sample collectors were used: a sapphire crystal and a glass tip. The former was used in the preliminary experiments and the spectra obtained with it invariably consisted of two strong triplets, one centered near the free-atom resonance absorption and one shifted about 500 Å to the blue. Our results for sodium in argon on the sapphire are identical

TABLE I. Observed absorption maximum of A centers and the line splittings. In each case $\bar{E}$ is the unweighted average of the three components of the triplet.

	Ar		Kr		Xe	
	λ (Å)	$\bar{E}-E_i$ (cm^{-1})	λ (Å)	$\bar{E}-E_i$ (cm^{-1})	λ (Å)	$\bar{E}-E_i$ (cm^{-1})
Na	5947±10	−290				
	5860±10	−40				
	5737±15	+330				
K	7754±10	−270	7922±20	−290	8049±20	−265
	7640±15	−80	7729±20	−10	7882±20	0
	7400±25	+350	7567±20	+300	7721±20	+265
Rb	7923±10	−310				
	7742± 7	−15				
	7542± 7	+325				
Cs	8893± 6	−486	9061±25	−462	9253±40	−423
	8466± 5	+80	8671± 5	+31	8897±10	+10
	8240± 5	+406	8378±15	+431	8589±25	+413

with those of McCarty and Robinson.[6] The "shifted" triplet was slightly more intense. The subsequent use of the glass tip brought about an order-of-magnitude reduction in the intensity of the shifted triplet, while the unshifted one remained at least as strong as on the sapphire. There was no discernable change in the relative intensities of the individual components of any particular triplet. We believe this supports the suggestion that the individual triplets are due to the absorption of impurities in different sites. As all the impurity-matrix combinations were studied on the glass tips but not on the sapphire, we shall present results for the unshifted site only.

Table I summarizes the measured absorption maxima. The shifts of the lines, $\bar{E}-E_i$, are measured from the unweighted average $\bar{E}$ of the three components of the triplet. The use of the unweighted average assumes that the observed splitting into three components is caused by the lattice removing the threefold degeneracy due to the angular momentum of the excited P state. The wavelength assignments have been corrected for the spectral response of the system but not for the shape distortion due to overlap of neighboring components. Figure 4 shows in a graphical form the relative splittings of the triplet for Na, K, Rb, and Cs in an argon matrix as a function of the spin-orbit splitting of the P state of the free atom. Figure 5 shows the relative splittings for Cs and K in argon, krypton, and xenon gas matrices.

The full width at half-maximum of the absorption lines was estimated from the apparent resolution of the components to decrease from 350 cm^{-1} for sodium in argon to 200 cm^{-1} for cesium in argon. An attempt was made to see if these centers recognize circularly polarized light. The spectrum of cesium did not change to the extent of 10% in a field of 20 G parallel to the polarized light beam. Several runs were made to determine the temperature dependence of the linewidths; however, the samples could not be stabilized at a temperature high enough to see any effect.

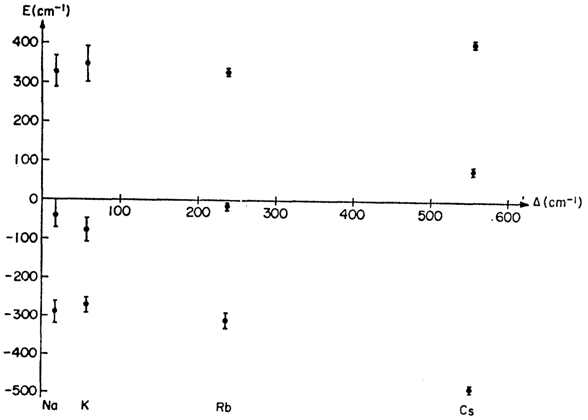

FIG. 4. Crystalline-field splittings of alkali atoms in an argon matrix as a function of the free-atom splitting, Δ. In each case $\bar{E}_{\text{solid}}$ was taken to be zero.

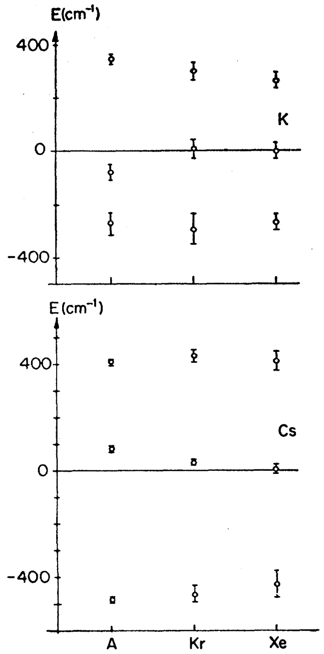

FIG. 5. Crystalline-field splittings of potassium and cesium atoms in different inert matrices. In each case $\bar{E}_{\text{solid}}$ was taken to be zero.

INTERPRETATION

The similarity of the spectra for the various combinations of alkali-metal atom and rare-gas matrix suggests that there may exist a simple explanation for the observed spectra. In this section we shall attempt to derive such an explanation.

The free alkali atoms have a ${}^2S_{1/2}$ ground state and a doublet first excited state whose term assignments are ${}^2P_{1/2}$ and ${}^2P_{3/2}$. The excitation energy of the first P state is 2–3 eV for all the alkali elements. Table II summarizes the wavelength of the S–P alkali metal transitions and the spin-orbit splittings of the P states. The rare gases crystallize in the form of a face-centered cubic system; Table III summarizes the lattice constants for the various gases. The inert gas atoms have no mechansim by which they can strongly attract an additional electron; they consist of tightly bound closed shells whose first excited state is a single electron excita-

TABLE II. The resonance lines and spin-orbit splittings for the free alkali metal atoms.

	λ ${}^2P_{1/2}\rightarrow{}^2S_{1/2}$ (Å)	λ ${}^2P_{3/2}\rightarrow{}^2S_{1/2}$ (Å)	Δ (cm^{-1})
Na	5895.92	5889.95	17.19
K	7698.98	7664.91	57.74
Rb	7947.60	7800.23	237.72
Cs	8943.50	8521.10	554.27

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[6] M. McCarty and G. W. Robinson, Mol. Phys. 2, 415 (1959).

TABLE III. The lattice spacing and internuclear distances for the rare gases at 4.2°K.

	Lattice constant (Å)	Internuclear distance (Å)
Ar	5.312	3.76
Kr	5.644	3.99
Xe	6.131	4.33

tion about 10–15 eV above the ground state. The depth of the attractive potential due to the Van der Waals force is about 0.02 eV for a sodium-argon pair. These facts suggest that the alkali impurity in an inert-gas matrix is a tightly bound center, similar in many respects to the *F* centers in alkali-halide crystals. The experimental results show that the energy involved in the resonance transition is similar in the two cases; the *A* centers, however, have narrower lines and a resolvable structure. We shall assume these impurities are a new type of tightly bound color center and proceed to interpret them along conventional lines. That is, we shall use the configuration coordinate scheme to deal with the energy shifts and the linewidths, and the crystalline-field approach to explain the level splittings.[1]

Two fundamental tenets underlie our interpretation. The first is that the transition involved in the absorption corresponds to the free-atom *S*- to *P*-state transition and that these states maintain their character when the atom is in the matrix. The second is that the observed triplet is due to the lifting of the degeneracy of a single electron state and is not due to atoms in different sites. This latter point is supported by the observation that we could change the relative intensities of two such triplets by changing the plating conditions but could not change the internal structure of either triplet.

Lax[7] has shown that if the impurity is at a temperature which is low compared to the Debye temperature of the solid and if the transition is to a high vibrational level of the final state (vibration quantum number $\gtrsim 50$), the processes of absorption and emission can be treated as a semiclassical problem, i.e., the initial state is treated qunatum mechanically and the final state is treated classically. In this case one assumes that only the zeroth vibrational level of the gound state is populated and treats the lattice motions in the final state classically.

Lax[7] has also shown that any given lattice motion can be represented parametrically by a single normal mode coordinate called the configuration coordinate. The approximation usually made in the literature is to consider the dominant mode of vibration to be the "breathing mode," i.e., the mode in which the crystal expands and contracts isotropically about the impurity. The configuration coordinate Q in this approximation is just the internuclear distance between the impurity and one of the adjacent matrix atoms. We then replace the impurity surrounded by the matrix by an impurity atom interacting with a single particle having an effective mass M and situated a distance Q from the impurity. The effective mass is very nearly the sum of the masses of the nearest-neighbor impurity atoms and the interaction potential is the net potential of the impurity atom in the matrix. The breathing-mode approximation is probably quite accurate for an impurity in an initial S state; for an initial state with angular momentum, however, the interaction with the crystal must be anisotropic and the application of this approximation is questionable.

We proceed now, on the basis of this model, to derive expressions for the linewidths in terms of pair potentials.[8] Let M be the sum of the masses m_1 of the n nearest neighbors and the potential be $nV(r)$, where $V(r)$ is the impurity-matrix pair potential. Figure 6 shows a typical configuration coordinate diagram of a transition between two impurity electronic states, labeled g and e. We shall only discuss the absorption transition.

When we spoke previously about treating the excited state classically, we meant that the electrons make transitions only to points on the excited-state potential curve, rather than to intermediate points on a vibrational level such as point c in the diagram. We also have only vertical transitions as required by the Franck-Condon principle. For this situation the line shape is a simple function of the gound-state distribution of the electrons in the one-dimensional Q space. Thus

$$W = n(dV_e/dQ)\Delta Q\,, \qquad (1)$$

where ΔQ is the full width at half-maximum of the electron distribution in the ground state and Q_0 is the equilibrium coordinate. This assumes that ΔQ is sufficiently small that the slope of nV_e changes little in this interval.

To calculate ΔQ we approximate the ground-state

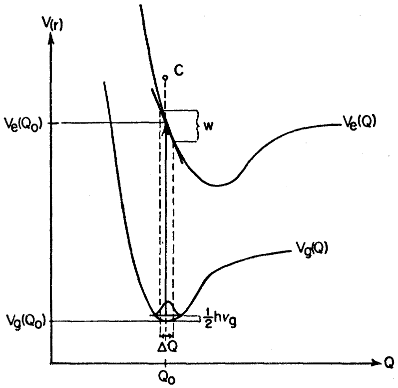

FIG. 6. Conjugate coordinate diagram for absorption. This diagram is schematic and not drawn to scale.

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[7] M. Lax, J. Chem. Phys. **20**, 1752 (1952).

[8] C. C. Klick, D. A. Patterson, and R. S. Knox, Phys. Rev. **133**, A1717 (1964). This article gives a general discussion of the limitations of the configuration coordinate treatment of certain *F* centers.

potential about Q_0 by a simple harmonic oscillator whose force constant is

$$k_g = n \left.\frac{d^2 V_g}{dQ^2}\right|_{Q=Q_0}. \tag{2}$$

We can avoid using the ground-state potential by noting that $\omega_g{}^2 = k_g/M$ and taking ω_g to be given by the Debye relation

$$\bar{\omega} = (\tfrac{3}{5})^{1/2}(k\theta_0/\hbar). \tag{3}$$

Here θ_0 is the Debye temperature and k and $\hbar$ are the Boltzmann and Planck constants, respectively. The ground-state distribution as a function of Q is given by the ground-state harmonic-oscillator wave function. This distribution is

$$|\psi|^2 = (\alpha/\pi^{1/2})e^{-\alpha^2(Q-Q_0)^2}, \tag{4}$$

where $\alpha = (m\omega_g/\hbar)^{1/2}$ and ω_g is the angular frequency of the corresponding classical harmonic oscillator. From this we find that

$$\Delta Q = 2(\ln 2)^{1/2}(\hbar/M\omega_g)^{1/2}. \tag{5}$$

Equation (1) for the linewidth then becomes

$$W^2 = 4(\ln 2)(\hbar/M\omega_g)[n(dV_e/dQ)]^2 \tag{6}$$

$$= 4(\ln 2)(\hbar/M\bar{\omega})[n(dV_e/dQ)]^2. \tag{7}$$

The shift in the transition energy from the free-atom value can be written down by inspection of Fig. 6. It is

$$\Delta E = V_e(Q_0) - V_g(Q_0) - \tfrac{1}{2}\hbar\omega_g. \tag{8}$$

This assume that the two potential functions are equal to zero when the atoms are very far apart.

For the necessary potentials we shall use the Lennard-Jones 6-12 form of potential which can be written in either of the two convenient forms

$$V(r) = C_{12}/r^{12} - C_6/r^6, \tag{9}$$

or

$$V(r) = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6], \tag{10}$$

where ϵ is the depth of the well and σ is the effective size of the cores, i.e., the internuclear distance below which the interaction is repulsive. By using known values of C_{6g}, σ_g, and $(C_{6e} - C_{6g})$, Bergeon[9] fitted the data of Robin *et al.*[10] for the optical absorption spectrum of sodium in high-pressure argon to a Margenau-type statistical model of spectral broadening and shifting to obtain the fourth parameter. For the 6-12 sodium-argon potentials, Bergeon gives

$$V_g = 19.7\times10^8/r^{12} - 9.68\times10^5/r^6 \text{ cm}^{-1},$$

$$V_e = 390\times10^8/r^{12} - 27.6\times10^5/r^6 \text{ cm}^{-1}.$$

Here r is in Å. Using these potentials, the observed Debye temperature of 93.3°K for argon, $n=12$, and the experimental value of $W = 350$ cm^{-1} for sodium A centers, we find that $Q_0 = 4.7$ Å. From the observed energy shift, $\Delta E = 0$, we obtain $Q_0 \approx 4.9$–5.0 Å. The configuration coordinate Q_0, calculated from the width decreases by 0.1 Å as the number of nearest neighbors decreases to six; it remains unchanged for the energy shift calculation since the shift is taken to be zero. These numbers should be compared with the known argon-argon separation in the crystal of 3.8 Å. For sodium in a substitutional site, these potentials give $\Delta E = +40\,000$ cm^{-1} and $W = 9000$ cm^{-1}. It is difficult to assess the validity of these calculations, especially when the separation decreases and the electronic structures overlap. Nevertheless, surprising agreement for Q_0 between the two calculations has been obtained. A potential derived from low-pressure data and simple calculations gave a discrepancy of 1.5 Å: 4.4 Å derived from W and 5.9 Å from $\bar{E}$. These calculations suggest that the sodium is not in a substitutional site but that more than one argon atom is missing from the lattice. If the sodium is centered in the vacancy left by two missing nearest neighbors, the site has a twofold symmetry.

On the basis of the results of the previous section, we shall assume that the alkali impurities we are observing are not in substitutional sites and that the crystal is distorted in the neighborhood of the impurity. We shall now apply the standard theory of crystalline fields and ask if the observed splittings can be explained by a field which is roughly the same for all the A centers observed. This calculation should be regarded as a means for obtaining a schematic representation of the data.

Since the S and P states involved in this transition are well separated from other excited states in the free atom, we shall assume that the crystalline field mixes in negligible amounts of the other states. The splitting is then solely due to the action of the field on the P state.

In general, the electrostatic potential about a point impurity can be written in the form

$$V = \sum_{l} \sum_{m=-l}^{l} A_l{}^m Y_l{}^m(\theta,\phi). \tag{11}$$

We must deal with matrix elements within the P state of the form

$$\int \psi_1{}^{m_1} V_l{}^m \psi_1{}^{m_2} d\tau. \tag{12}$$

The terms with l odd vanish because the integral changes sign under an inversion of the coordinate system; the terms with $l > 2$ are zero because of the orthogonality of the spherical harmonics; the term $A_0{}^0$ is a constant and produces a shift rather than a splitting.[11] If, in addition, we require that the potential be real we

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[9] R. Bergeon, thesis, University of Paris, 1958 (unpublished).

[10] J. Robin, S. Robin, and B. Vedar, Compt. Rend. **232**, 1754 (1951).

[11] E. Fick and G. Joos, *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1957), Vol. XXVIII, pp. 205–295.

TABLE IV. The crystalline-field parameters a_2^0 and a_2^2, for the A centers in the various rare-gas matrices. All the energies are in units of cm^{-1}.

		Ar			Kr			Xe		
		I	II	III	I	II	III	I	II	III
Na	a_2^0	−160	1310	−1190						
	a_2^2	1000	405	600						
K	a_2^0	−325	1380	−1060	−40	1180	−1140	0	1040	−1040
	a_2^2	1000	300	695	950	450	500	850	425	425
Rb	a_2^0	−120	1190	−1070						
	a_2^2	925	385	540						
Cs	a_2^0	130	1200	−1320	−280	1360	−1070	Imaginary solutions only		
	a_2^2	1020	590	440	990	320	665			

can write, without loss of any meaningful terms

$$V=a_2^0Y_2^0+a_2^1(Y_2^1+Y_2^{-1})+a_2^2(Y_2^2+Y_2^{-2}). \quad (13)$$

This potential has three adjustable parameters; we only have two independent experimental measurements, the two line splittings. Thus to make a solution possible we must simplify the problem. We shall assume that the field possesses twofold symmetry about the axis defined by the a_2^0 term. In this case,

$$V=a_2^0Y_2^0+a_2^2(Y_2^2+Y_2^{-2}). \quad (14)$$

Such a potenital is equivalent to a decomposition of the field into terms of cubic and rhombic symmetry. The site in which two nearest-neighbor argon atoms are replaced by an alkali atom is described by this potential.

Since this field may be large, we cannot treat it as a perturbation on the spin-orbit coupled states of the free atom but must add in the spin-orbit coupling as a separate interaction. Thus we treat the excited state as a hydrogenic state wtih the perturbation Hamiltonian

$$H=V(\theta,\phi)+\lambda\mathbf{l}\cdot\mathbf{s}. \quad (15)$$

Here λ is the spin-orbit coupling constant for the free atom. Table IV lists the solutions for this problem. Unfortunately all of the solutions of the cubic equation are real, so other experimental means for distinguishing them must be sought. The solution for Cs in Xe is only slightly imaginary in the sense that shifts of the data within the quoted error or a slight decrease in the spin-orbit coupling constant are sufficient to make it real. It has been pointed out to us that reductions of the spin-orbit coupling constant from the free-atom values are sometimes required to obtain agreement between theory and experiment in such solids.[12] The similarity of the solutions as the impurity-matrix combination is varied is striking. This indicates that the nature of the interaction which produces the splitting is uniform in all cases but leaves open the question as to whether the origin of the interaction is static or some dynamic interaction such as the Jahn-Teller effect. The theoretical work of Fowler and Dexter implies that it is a static interaction.[13]

CONCLUSIONS

The resonance absorption of alkali impurities in inert-gas matrices has been observed and the basic characteristics measured. The general features of the spectra can be described in terms of conventional theory with no major discrepancies. On the other hand, not enough information is yet available for a detailed model to be constructed.

A simple vacancy model could explain the results obtained so far. If the alkali impurity deposits in a substitutional site with one or more nearest-neighbor vacancies, the average equilibrium separation Q_0 would be greater than the lattice constant and a large crystalline field splitting of the excited P state would result. In order to test this, it is important to obtain a correlation between the lines in the optical and microwave absorption spectra. Observations of the fluorescence spectrum of the A centers and of the temperature dependence of the line width would further clarify the configuration coordinate model.

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