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Excitonic and molecular spectra of rare gases*

R. A. Tilton† and C. P. Flynn

Department of Physics and Materials Research Laboratory, University of Illinois, Urbana, Illinois 61801

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From a comparison of rare-gas pair excitation spectra in metals with the absorption spectra of rare-gas solids it is suggested that the optically accessible exciton states of rare-gas crystals have a basically diatomic structure. A specific form is suggested for the exciton wave function.

I. INTRODUCTION

The interactions among rare-gas atoms occupying their ground states usually conform quite well to simple dispersion force models,[1,2] although clathrate formation[3] and true molecular bonding[4] do occur in some cases. In contrast, excited rare-gas atoms interact strongly as both the electron and the hole can take part in bonding. Only Ne_2 has been subjected to detailed theoretical study.[5] Strong spin-orbit coupling adds complexity for heavy rare gases, and only a semiempirical study of Xe_2 by Mulliken[6] is available.

Excitation spectra of the solid rare gases, published by Baldini,[7] show sharp exciton lines and other features that have been discussed using band models.[8] Electronic carriers do propagate freely[9,10] but the holes are now known to self-trap, most probably as diatomic molecules.[11,12] Self-trapping can be expected even in the absence of such covalency[13] and exciton models have focused on holes trapped at one atom.[14–16] It is suggested in what follows that this emphasis may be incorrect, and that the optical excitation process leads directly to diatomic excitons.

Impurities in rare-gas crystals offer further complexities and rich spectra not clearly related to excitonic structure in the pure lattices of either the host or impurity species.[7,17,18] Results are also available for deep core holes,[19,20] but a comprehensive interpretation of all these "persistence"[21] impurity absorption spectra is still lacking. Luminescence spectra from rare-gas alloys have, however, been identified unambiguously with emission from both homoatomic and heteroatomic rare-gas pairs.[22] These lines are Stokes's shifted from the absorption lines and it could be thought that lattice relaxation provided the dominant mechanism responsible for diatomic emission. It is suggested here that this may not be the case, since the oscillator strengths for absorption in the undeformed crystal appears to resemble a superposition of components each associated with one pair of nearest-neighboring rare-gas atoms.

II. DISCUSSION

Some selected optical spectra for rare-gas impurities in potassium are reproduced[23] in Figs. 1(a)–3(a). Each figure shows a curve for high-impurity concentration c superposed on the limiting curve for $c \rightarrow 0$. The sharp structure in the difference is ascribed in Ref. 23 to absorption principally by pairs of rare-gas atoms occupying neighboring sites in the metal host lattice; the three cases pertain, respectively, to Xe_2, Kr_2, and XeAr diatomic centers. Figures 1(b)–3(b) show for purposes of comparison the absorption spectra of thin films of pure Xe, pure Kr, and of Ar containing ~0.1-at.% Xe.[7] A central point in this discussion is that the sharp features in the

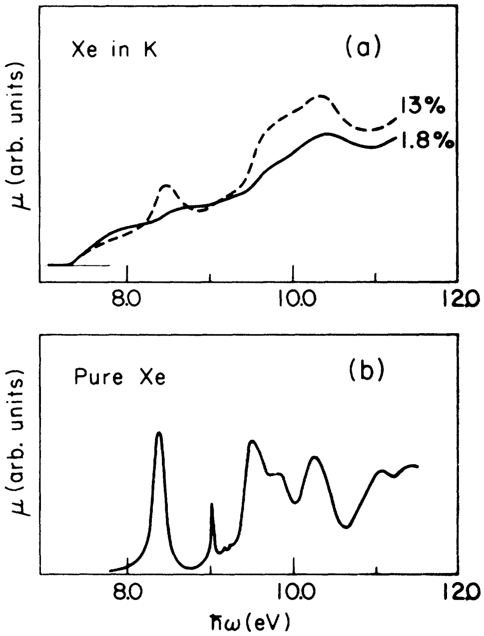

FIG. 1. (a) Spectrum of Xe at two concentrations in K. Differences between these curves arise principally from random pairing at higher concentrations, and are to be compared with the spectrum of pure solid Xe in (b).

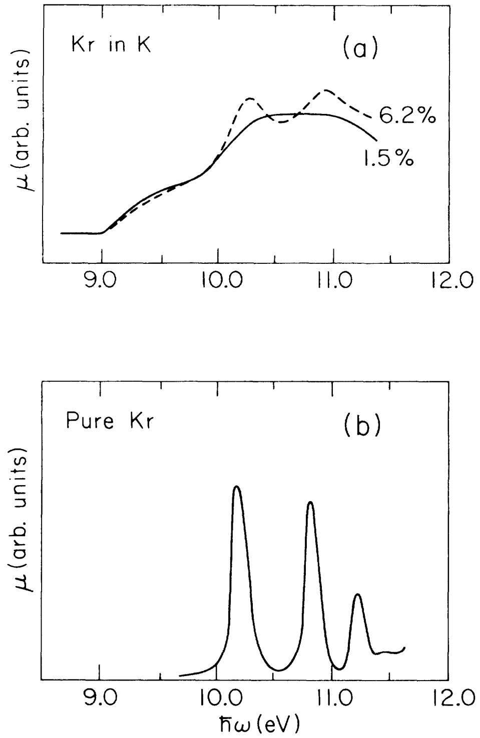

FIG. 2. (a) Spectrum of Kr at two concentrations in K. Differences between these curves arise principally from random pairing at higher concentrations, and are to be compared with the spectrum of pure solid Kr in (b).

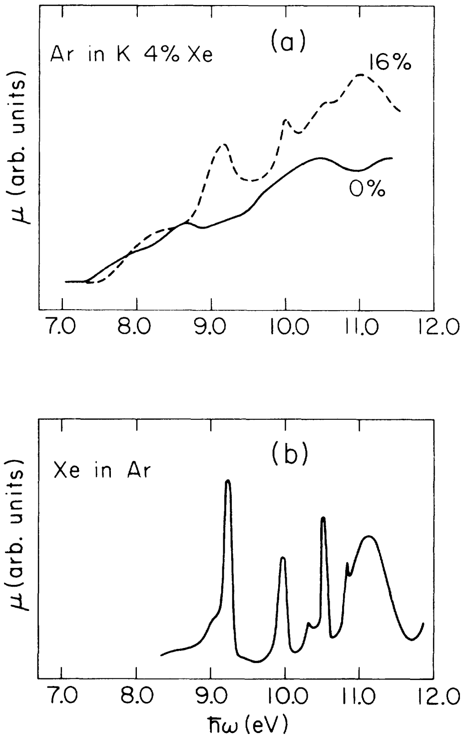

FIG. 3. (a) Spectrum of Xe at 4-at.% concentration in K for two concentrations of additional Ar doping. Differences between these curves arise principally from random pairing of Xe with Ar and are to be compared with the spectrum of Xe at dilution in Ar, shown in (b).

metal spectra fall close to prominent lines in the rare-gas spectra. The positions of rare-gas lines in various host lattices are compiled in Table I.

The absorption spectra of homoatomic and heteroatomic rare-gas pairs have not yet been observed, but there are good reasons to believe that they resemble the pair spectra of the metallic alloys. In passing from the lightest alkali metal, Li, to the heaviest, Cs, the host electron density decreases by a factor ~5. Nevertheless, the pair peaks exhibit only minor shifts. The pair peaks are sharp and show no signs of quasiparticle pair creation processes from coupling to the surrounding metal (see Table I). This insensitivity to electronic environment suggests that no major spectral changes can be expected in passing from the Cs host to zero electron density thus isolating the spectrum of the diatomic molecules in vacuum. We shall presume in what follows that this is the case, although the molecular spectra are not available to verify this deduction.

A natural explanation of the similar features observed in these pair spectra and the solid rare gases is now that *both* contain principal components derived from the diatomic molecular spectrum. The alternative explanation, that rare-gas atoms cluster into local regions of rare-gas solid in the metal, is not consistent with the experimental evidence.[24] In the cases of pure Kr and pure Xe the exciton lines of the solid hosts also fall close to resonance levels of the isolated rare-gas atoms. Their coincidence with pair lines in metals therefore does not provide definitive evidence for pairing effects in solid rare gases. For the XeAr results this ambiguity does not exist. The low-energy XeAr pair lines coincide with neither the resonance lines of isolated Ar nor Xe atoms; rather, they conform only to the spectrum of Xe in dilution in Ar. These data therefore *do* provide strong evidence that the oscillator strength in the solid rare gases is somehow disposed in a pairwise fashion. Our remaining discussion will center on the implications of this unexpected result, and on the nature of exciton spectra when the molecular splittings exceed the instantaneous phonon splittings.

Electronic localization in an otherwise translationally invariant system normally occurs through coupling between the excited electrons and the phonon system of the host. It is in principle well understood in many cases, such as V_k centers in salts, which show molecular pairing effects rather

TABLE I. Energies (in eV) of Xe_2, Kr_2, and XeAr pair peaks in alkali-metal hosts and in solid rare gases. The last column (rare gas) gives prominent lines of Xe in Xe, Kr in Kr, and Xe at dilution in Ar. Only for Xe in K (marked*) has the apparent concentration dependence been extrapolated to $c = 0$ from the typical measurements at $c \sim 2$ at.%.

	Li	Na	K	Rb	Cs	Rare gas (Ref. 7)
Xe$(P_{3/2})$	8.58	8.57	8.68*	8.52	8.50	8.36
Kr$(P_{3/2})$	10.37	10.39	10.36	10.33	10.34	10.17
Kr$(P_{1/2})$	11.00	11.11	11.02	11.00	10.95	10.81
Xe-Ar(1)	···	···	9.13	···	···	9.22
(2)	···	···	9.94	···	···	9.97
(3)	···	···	10.44	···	···	10.53

similar to those suggested here for rare gases.[13] However, self-trapping by *static* phonon displacements plays a central part in electronic localization of the V_k center, and is mainly responsible for the observed degradation of electronic propagation into incoherent hopping between translationally equivalent sites.[25] Large displacements of this type *cannot* be present in the lattice configurations accessible to rare gases during low-temperature absorption spectroscopy. Any pairwise disposition of oscillator strength evident in the spectra therefore requires a different explanation.

There are now available fairly clear indications that a hole suddenly created in a rare-gas lattice cannot be confined to one site. Detailed calculations for the Ne_2^+ molecule ion[5] reveal splittings of the free atom levels by ~50 meV at the spacing relevant to solid Ne in equilibrium. The total splittings arise from comparable contributions from the coupling of angular momenta to the molecular axis and from tunnel splitting by excitation transfer between the component atoms. Both components exceed typical phonon energies for the solid by a factor ~5. One therefore deduces that a hole, suddenly created in the valence band of the solid can and will transfer from one atom to the next in a time corresponding to a fraction of one phonon period, even if the sites are nonequivalent by several phonon energies. The appropriate hole states are thus somewhat delocalized and probably contain components derived from various molecular splittings.

Splittings and couplings very similar in magnitude to those for Ne_2^+ are calculated for the neutral Ne_2 excited molecule constrained to the interatomic separation of the solid. For this reason the optical excitations accessible to the solid at low temperatures probably also spread to more than one site and have components corresponding to various molecular couplings. We note that molecular couplings of the relevant type are neglected in simplified exciton models that have the electron orbiting in the lattice near a hole possessing a *fixed* total angular momentum and located on one atom.[14-16] This is the model employed in the most realistic available calculations of exciton states in rare gases.

Certain complexities attend efforts to define precisely the extended optically accessible exciton states of rare-gas lattices in the presence of an instantaneously irregular lattice and strong electron-lattice coupling. To the neglect of interactions with the radiation field, which introduce blurrings probably $\lesssim 10$ μeV, there do exist exact vibronic eigenstates, however complex, containing coupled electronic and lattice coordinates. To the extent that the excitons do finally trap as diatomic molecules,[22] the exact vibronic states must, without question, comprise a superposition of diatomic moleculelike parts, each carrying with it a self-consistent description of the relatively unexcited electronic system of the remaining atoms at the instantaneous lattice coordinates. The feature introducing difficulty is that optical absorption occurs near lattice coordinates for which alternative neighboring configurations of the diatomic center are nearly degenerate and could possibly mix to regain some of the translational symmetry of the perfectly regular lattice. Sufficiently large mixing matrix elements of this type break down the basic diatomic form of the local electronic structure and thereby remove the moleculelike disposition of oscillator strength from the optically accessible spectrum. Qualitatively, it is clear that intramolecular tunneling is not *very* much faster than typical phonon frequencies, so the superposition of electronic components reached by optical processes must comprise resonances that are spatially quite localized. It remains to be determined whether or not the interactions among alternative molecular components within this localized region are strong enough to break down molecular couplings.

In the case of impurity excitons it is possible to be quite specific by presenting two extreme choices for the exciton wave function. The first choice has been employed in the literature to investigate rare-gas excitons[15,16,26]

$$\Psi=\psi_h\psi_e\ , \tag{1}$$

in which ψ_h is an atomiclike hole state localized on one atom while ψ_e represents the electron orbiting in the combined hole and lattice field. The alternative choice we propose here starts with molecular wave functions $\phi_{\alpha n}$ for the αth molecular state of the impurity interacting with the near neighbor labeled by n. The first approximation to the ith wave function is then

$$\Psi_i(\vec{Q})=\sum_{n\alpha}\gamma_{\alpha n i}(\vec{Q})\phi_{\alpha n}(\vec{Q})\ , \tag{2}$$

in which the dependence on the instantaneous lattice coordinates $\vec{Q}$ is indicated explicitly, using the Born-Oppenheimer approximation for individual vibronic components. In principle, the coefficients $\gamma(Q)$ are to be determined by diagonalizing the Hamiltonian in some approximation, but in the absence of available molecular wave functions this does not appear feasible even for periodic lattices at present. One may nevertheless ask whether the available evidence indicates that Eq. (2) represents a suitable choice of wave function or whether, to the contrary, basic states of the form given in Eq. (2) are so intermixed in higher approximations that the diatomic features are largely obliterated and Eq. (1) is to be preferred.

The experimental evidence under discussion in this paper appear to cast fresh light on this question. This is particularly the case for the data concerning XeAr interactions. For this case these data seem to provide unambiguous evidence that the exciton wave functions possess energy levels closely related to the diatomic molecular form given by Eq. (2), so that this form is to be preferred over the customary choice represented by Eq. (1). The data for homoatomic pairs are consistent with a similar conclusion, but the coincidence of the pair lines with the resonances of isolated rare-gas atoms introduces ambiguities into the interpretation of these cases.

One further point that warrants mention here concerns the detailed vibronic description of hole and exciton states in rare gases. These may differ in one important respect. Mulliken[6] first drew attention to the possible presence of potential barriers in the interatomic potential for Xe_2^* that are absent for $(Xe_2^-)^*$. For Ne these features are reproduced in detailed calculations of the Ne_2^* energy.[5] It is therefore possible that, in some or all the rare-gas solids, the suddenly created hole can pass directly into the self-trapped state within very few phonon periods. In contrast, the potential barrier present in the interatomic potential for the essentially diatomic excitons proposed herein may lend the exciton some transient stability against immediate trapping. A final elucidation of the dynamics must, of course, await detailed studies.

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[†] Present address: Laboratory of Atomic and Solid State Physics, Clark Hall, Cornell University, Ithaca, N. Y.

[1] F. London, Z. Phys. 63, 245 (1930).

[2] G. K. Horton, Am. J. Phys. 36, 93 (1968).

[3] See, for example, J. H. Holloway, *Noble-Gas Chemistry* (Methuen, London, 1968).

[4] See, for example, J. H. van der Waals, Trans. Faraday Soc. 52, 184 (1956).

[5] J. S. Cohen and B. Schneider, J. Chem. Phys. 61, 3230 (1974).

[6] R. S. Mulliken, J. Chem. Phys. 52, 5170 (1970).

[7] G. Baldini, Phys. Rev. 128, 1562 (1962); 137, A508 (1965).

[8] J. C. Phillips, Phys. Rev. 136, A1714 (1964).

[9] L. S. Miller, O. Howe, and W. E. Speare, Phys. Rev. 166, 871 (1968).

[10] W. E. Speare and P. C. LeComber, Phys. Rev. 178, 1454 (1969).

[11] H. D. Pruett and H. P. Broida, Phys. Rev. 164, 1138 (1967).

[12] P. G. Le Comber, R. J. Loveland, and W. E. Speare, Phys. Rev. B 11, 3124 (1975).

[13] W. B. Fowler, Phys. Rev. 151, 657 (1966); *Physics of Color Centers* (Academic, New York, 1968).

[14] R. S. Knox and F. Bassani, Phys. Rev. 124, 652 (1962); and the erratum in R. S. Knox, Proceedings of the Colorado Springs Symposium on Excitons, May 1962 (unpublished).

[15] S. Webber, S. A. Rice, and J. Jortner, J. Chem. Phys. 41, 2911 (1964); 42, 1907 (1965).

[16] A. Gold, Phys. Chem. Solids 18, 218 (1960); Phys. Rev. 124, 1740 (1961).

[17] N. Nagasawa, T. Karasawa, N. Miura, and T. Nanba, J. Phys. Soc. Jpn. 32, 1155 (1972).

[18] R. Haensel, N. Kosuch, U. Nielsen, B. Sonntag, and U. Rossler, Phys. Rev. B 7, 1577 (1973).

[19] R. Haensel, G. Keitel, E. E. Koch, M. Skibowski, and P. Schreiber, Phys. Rev. Lett. 23, 1160 (1969); R. Haensel, G. Keitel, C. Kunz, and P. Schreiber, *ibid.* 25, 208 (1970).

[20] F. C. Brown, C. Gähwiller, H. Fujita, N. Carrera, and W. Scheifley, Mem. Soc. R. Sci. Leige 8° (Belgium, 1970), Vol. 5, No. 20, pp. 155-67.

[21] Y. Onodera and Y. Toyozawa, J. Phys. Soc. Jpn. 24, 341 (1968).

[22] A. Gedanken, J. Jortner, B. Raz, and A. Szöke, J. Chem. Phys. 57, 3456 (1972); A. Gedanken, B. Raz, and J. Jortner, *ibid.* 59, 1630 (1973); 59, 5471 (1973);

O. Cheshnovsky, B. Raz, and J. Jortner, *ibid.* 59, 3301 (1973); 59, 5554 (1973).

[23] R. A. Tilton, D. J. Phelps, and C. P. Flynn, second preceding paper, Phys. Rev. B 14, 5265 (1976).

[24] See, D. J. Phelps and C. P. Flynn, preceding paper, Phys. Rev. B 14, 5279 (1976).

[25] For a discussion of these processes see C. P. Flynn, *Point Defects and Diffusion* (Oxford, U.P., Oxford, 1972).

[26] See, e.g., R. K. Bhargava and D. L. Dexter, Phys. Rev. B 1, 1 (1970).