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Emission Spectra of Deep Impurity States in Solid and Liquid Rare Gas Alloys

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We have measured the spectral distribution (in the region 1100–2000 Å) of the α excited luminescence from solid and liquid dilute rare gas alloys. Emission was observed from the lowest deep impurity state of xenon in liquid and in solid argon, which provides evidence for medium relaxation resulting in a "cavity" formation around the excited impurity in dense rare gases.

Recent work has established that Wannier exciton and deep impurity states are amenable to experimental observation in filled shell (large gap) insulators such as rare gas solids.[1] From the experimental point of view the work of Baldini and of others[2–4] has demonstrated that the optical spectra of rare gas crystals and of dilute rare gas alloys exhibit a Wannier series converging to the bottom of the conduction band. From the theoretical point of view these observations have been rationalized invoking pseudopotential theory.[5] The lowest deep exciton or impurity state corresponds to an intermediate type excitation which can be described either in terms of the modified Frenkel tight binding scheme subjected to large nonorthogonality corrections,[6,7] or alternatively in terms of the $n=1$ Wannier state subjected to large central cell corrections.[5,8] The higher deep exciton and impurity states characterized by the quantum numbers $n\geq 2$ are adequately described, within the framework of the effective mass approximation, by the well known hydrogenic equation for the envelope function.[9] Finally, it was experimentally demonstrated that the observation of Wannier states in dense rare gases is unaffected by "symmetry breaking" effects, and these states are amenable to observation in positionally disordered systems[10,11] (i.e., liquid rare gas) and in substitutionally disordered systems[12] (i.e., heavily substituted solid rare gas alloys). All this experimental information has been obtained by absorption and by reflection spectroscopy. Emission studies from Wannier states in large gap insulators will be of considerable interest. However emission from deep exciton states of pure solid and liquid rare gases (except possibly from solid Ne)[13] cannot be observed in view of an efficient exciton trapping process. Previous emission studies by Jortner *et al.*,[14] by Basov *et al.*,[15] by Surko *et al.*,[16] and by Stockton *et al.*[17] have established that the emission of pure solid Ar, Kr, and Xe and from liquid He, Ar, Kr, and Xe, results from the formation of an electronically excited rare gas molecule $Y_2^*({}^1\Sigma_u, {}^3\Sigma_u)\rightarrow 2Y({}^1S_0)$, which is analogous to the second continuum of rare gases[18] excited at moderate pressures ($p>100$ torr) by an electric discharge or by an optical light source.[19] We wish to report the observation of the emission spectra of deep impurity states in solid and liquid rare gas alloys. These spectroscopic data provide new information concerning medium relaxation around deep impurity excited states in filled shell insulators.

The emission from solid and liquid alloys of rare gases bombarded with α particles was monitored by a 0.3 m crossed Czerny–Turner spectrograph (McPherson 218). The light was detected by a converter consisting of a sodium salicylate coated Pyrex plate mounted in front of a EMI 9514S photomultiplier cooled to 220°K. Spectral emission data were obtained in the range 1100–3000 Å. Slitwidths between 0.5 and 2.0 mm were used resulting in resolution of 6.5–26 Å.

The optical cell[20] was characterized by a 1 cm path length. The 0.5 mC americium α source replaced the back window of the cell, while the front window consisted of a LiF plate 2 mm thick. The cell was mounted on a variable temperature cryostat (Ricor Ein-Harod). The temperature could be varied in the range 80–300°K and controlled within ±0.5°K.

Matheson research grade rare gases were used. The total impurity content of the Ar gas was less than 0.1 ppm. The major impurity content of the Kr gas consisted of 11 ppm Xe, 2 ppm N_2 and 1 ppm O_2. Rare gas Xe/Ar and Xe/Kr mixtures (Xe impurity doping level 5–2500 ppm) were prepared in a bakeable metal vacuum system connected to the optical cell, where an initial pressure of 10^{-6} torr was achieved prior to the introduction of the gas mixtures. The gaseous mixtures were then liquified in the cell at a pressure of 1000 torr. Doped solid rare gases were prepared by a moderately slow cooling (0.5°K/min) of the liquid under pressure of 1000 torr. This procedure resulted in optically transparent 1 cm thick solid Ar and Kr doped with Xe, which were perfectly suitable for emission studies. The Xe impurity content in the liquid and solid samples prepared by these procedures was assumed to be equal to that of the composition of the gaseous sample. Optical absorption studies of Xe/Ar and of Xe/Kr 1 cm thick liquid and solid matrices (Xe doping level 1–10 ppm) indicate that the Xe enrichment factor of the samples is less than ~ 2.

A general purity check of the system and of the gas handling procedure was performed by monitoring the vacuum uv emission spectrum of pure gaseous (pressure 1000 torr) liquid and solid Ar (Fig. 1). Small amounts (5–10 ppm) of impurities should diminish the intensity of the Ar_2^* emission continuum, where efficient energy transfer processes would result in the atomic and molecular emission of the impurities. The emission spectra of pure Ar at 1000 torr (Fig. 1) do not exhibit any impurity emission. A similar scan of the emission spectra of Matheson research grade "pure" gaseous krypton at 1000 torr (Xe impurity content 11 ppm) exhibited the Xe $^3P_1 \rightarrow {}^1S_0$ emission line superimposed on the broad Kr_2^* emission (which peaks at 1480 Å), thus demonstrating the efficient resonant energy transfer process from $Kr_2^*(^1\Sigma_u, {}^3\Sigma_u)$ to $Xe(^3P_1)$. The moral of this story is that reliable emission data from gaseous and dense rare gases and of their alloys can be obtained only from ultrapure samples. Thus the emission spectrum of "pure" liquid Ar (impurity content 0.05%) reported by Basov *et al.*[15] exhibits prominently the Xe_2^* emission band at 1740 Å rather than the Ar_2^* emission.

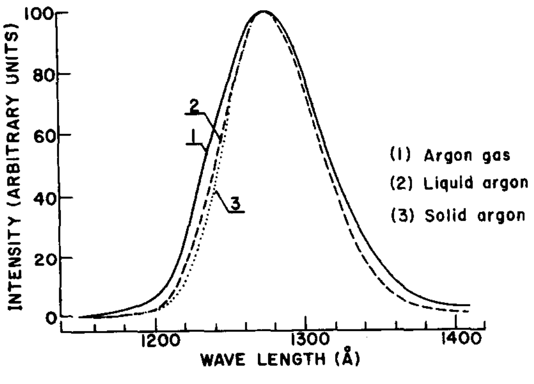

FIG. 1. Emission spectra of pure argon in gaseous (200°K), liquid (87°K) and solid (80°K) phase. Resolution 25 Å.

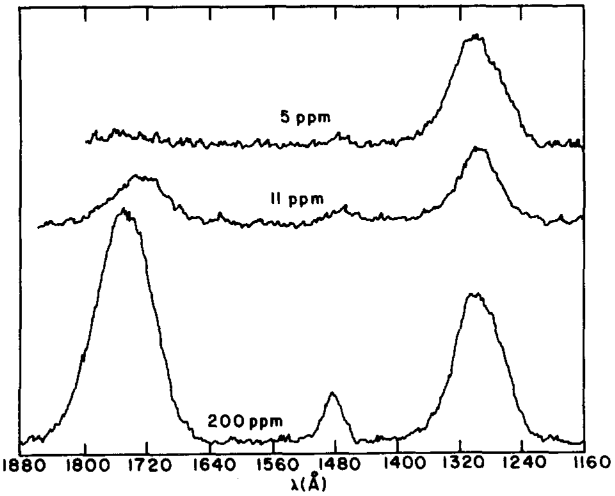

FIG. 2. Emission spectra of xenon doped liquid argon, at 87°K. Resolution 25 Å.

The emission spectra of liquid Argon doped with Xe [denoted by Xe/Ar(l)] and of solid Argon doped with Xe [i.e., Xe/Ar(s)] are displayed in Figs. 2 and 3, exhibiting the following emission bands:

(a) The Ar_2^* emission peaking at 1280 Å which diminishes in intensity with increasing Xe concentration due to energy transfer to the impurity. This emission is exhibited in gaseous, liquid, and solid phases, being unaffected by the state of aggregation of the medium.

(b) Liquid (and gaseous, $p \geq 500$ torr) Xe/Ar mixtures at $[Xe] > 10$ ppm (see Fig. 2) exhibit a broad emission band at 1720 Å, which practically coincides with the emission of pure Xe gas ($p \geq 100$ torr) and of pure liquid Xe.[14] This emission band in liquid Ar is assigned to the molecular emission of the Xe_2^* impurity molecule. This impurity molecular emission is absent in solid Xe/Ar up to $[Xe] > 200$ ppm (see Fig. 3).

(c) The emission bands observed at 1490±10 Å for Xe in liquid Ar and at 1480±10 Å for Xe in solid Ar are assigned to the emission from the lowest deep Xe impurity state $n=1$ $(^2P_{3/2})$. Stated in terms of the tight binding scheme these emissions correspond to the Xe $^3P_1 \rightarrow {}^1S_0$ transition. An alternative interpretation of these emission bands as originating from the XeAr* heteronuclear diatomic molecule is rejected on the basis of a study of the emission of Xe/Ar gaseous mixtures (temperature range 300–90°K) which in the spectral region of 1400–1600 Å exhibit only the Xe atomic emission.

The energy transfer processes in dense Xe/Ar matrices which result in the impurity emission can be

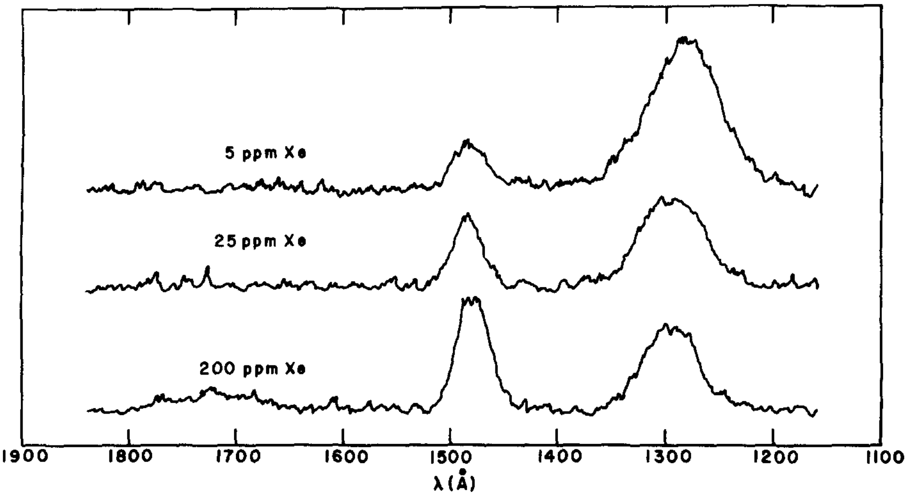

FIG. 3. Emission spectra of xenon doped solid argon at 80°K. Resolution 25 Å.

described as follows:

(1) Energy transfer from $Ar_2^*(^1\Sigma_u$ or $^3\Sigma_u)$ to the Xe impurity states via a long range energy transfer mechanism. This molecule-impurity atom energy transfer is induced by long range dipole-dipole coupling, the transition probability being determined by the transition moments of the donor and of the acceptor and by the spectral overlap between the donor emission and the acceptor absorption spectra.[21] Both for Xe/Ar(s) and for Xe/Ar(l) (see Figs. 4 and 5) energy transfer from Ar_2^* occurs predominantly to the dipole allowed Xe $n=1$ $(^2P_{3/2})$, Xe $n=2$ $(^2P_{3/2})$, and Xe $n=1$ $(^2P_{1/2})$ states.

(2) The higher Wannier impurity states $n\geq 2$ $(^2P_{3/2})$ decay nonradiatively to the lowest $n=1$ $(^2P_{3/2})$ state.

(3) The $n=1$ $(^2P_{1/2})$ state is unstable due to two nonradiative decay channels: It can (a) decay nonradiatively to the lowest $n=1$ $(^2P_{3/2})$ state (with the possible sequential participation of other excited Wannier states such as *np* type excitons) or (b) decay by autoionization to the conduction band. Subsequent electron-hole recombination will finally yield the $n=1$ $(^2P_{3/2})$ state.

(4) The Xe $(^3P_1)$ impurity state can be quenched nonradiatively to yield the metastable Xe $(^3P_2)$ state[22] which is dipole forbidden to the ground state. The energy gap between the Xe $(^3P_1)$ and the Xe $(^3P_2)$ impurity states should be close to the gas phase value (956 cm^{-1}).

(5) The Xe $(^3P_2)$ metastable impurity state yields the Xe_2^* $(^3\Sigma_u)$ excited molecule by collision with a ground state Xe $(^1S_0)$ atom.[18] This mechanism implies molecular diffusion and will be exhibited only in the liquid (and of course in the gaseous phase) but not in the solid. (The weak 1720 Å emission in heavily doped Xe/Ar(s) for [Xe]>200 ppm is due to Xe aggregation.)

(6) The observed emission of the Xe $n=1$ $(^2P_{3/2})$ (i.e., $^3P_1$) impurity state results from competition between the radiative decay of this dipole allowed state and Process (4).

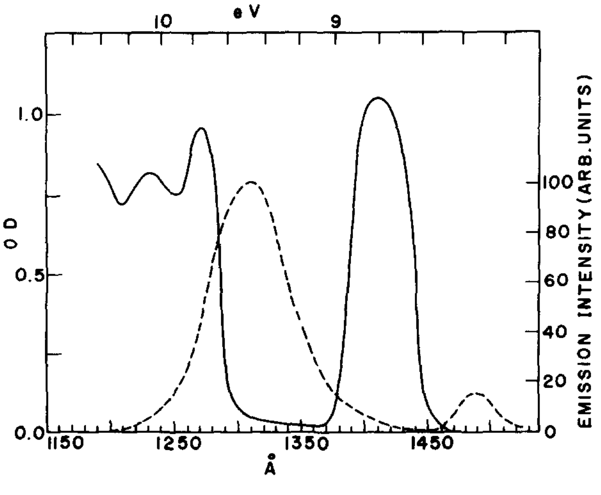

FIG. 4. Superposition of the absorption spectrum of xenon (1 ppm) doped liquid argon (full line)[10] and of the emission spectrum of 5 ppm Xe in liquid argon (dashed line).

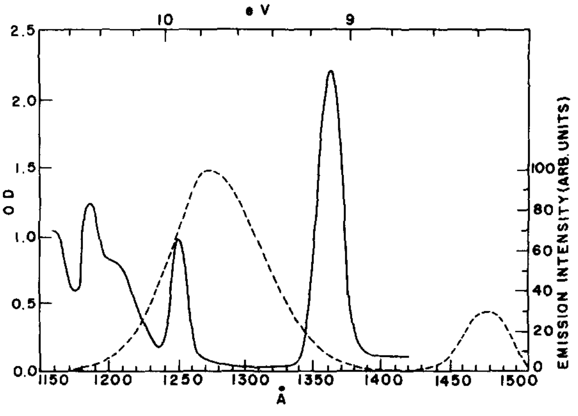

FIG. 5. Superposition of the absorption spectrum of xenon (1 ppm) doped solid argon (full line)[10,23] and the emission spectrum of 5 ppm Xe in solid argon (dashed line).

To conclude the exposition of our experimental results we would like to mention that we could not observe the emission from the Xe $n=1$ $(^2P_{3/2})$ impurity state in liquid and solid Xe/Kr mixtures. The emission spectra of these systems exhibit the following bands: (a) a broad emission band at 1480 Å, which diminishes in intensity with increasing Xe concentration (disappearing at 2000 ppm Xe), and is thus assigned to the host Kr_2^* $(^1\Sigma_u, {}^3\Sigma_u)$ emission, (b) a broad band at 1710 Å in liquid Kr but not in Xe/Kr(s) (for [Xe]<1000 ppm) which is assigned to the Xe_2^* $(^1\Sigma_u, {}^3\Sigma_u)$ diatomic impurity emission, and (c) a broad band at 1580 Å appearing both for Xe/Kr(l) and for Xe/Kr(s) and its intensity increases with increasing Xe concentration. A similar emission continuum was observed by us in gaseous Xe/Kr mixtures peaking at 1530 Å. Thus the 1580 Å band in Xe/Kr(l) and in Xe/Kr(s) is assigned to emission from a heteronuclear diatomic excited XeKr molecule.

We believe that our experimental results provide conclusive evidence for the observation of the emission from the lowest dipole allowed Xe impurity state, i.e., $n=1$ $(^2P_{3/2})$ (or $^3P_1$) level in solid and liquid Ar. No emission from higher impurity excited states $n\geq 2$ $(^2P_{3/2})$ or $n=1$ $(^2P_{1/2})$ was detected. From the comparison between the absorption spectra and the (α induced) emission spectra displayed in Figs. 4 and 5 we conclude that:

(a) A large red Stokes shift, ΔE_s, is exhibited for the $n=1$ $(^2P_{3/2})$ Xe impurity states being $\Delta E_s=5800\pm 200$ cm^{-1} for Xe/Ar(s) and $\Delta E_s=3630\pm 200$ cm^{-1} for Xe/Ar(l).

(b) The large Stokes shift observed for Xe/Ar(s) is consistent with the results of a recent spectroscopic study of the temperature dependence of the absorption linewidth corresponding to the impurity $^1S_0 \rightarrow {}^3P_1$ transition in this system.[23] From the investigation of the absorption spectra of 1 cm thick argon crystals doped with 1–5 ppm Xe Ophir has found[23] that the line shape of the $n=1$ $(^2P_{3/2})$ state is Gaussian, and the half-linewidth, H, varies from 1120 ± 10 cm^{-1} at 80°K to 750 ± 10 cm^{-1} at 33°K. The temperature dependence of the linewidth can be well fitted by the configurational diagram model within the framework of the harmonic single frequency approximation. The temperature dependence of the linewidth is given by $\mathrm{H}^2=(H_0)^2\coth(\hbar\omega/2k_BT)$, where ω is the effective phonon frequency and H_0 represents the linewidth at zero temperature. H_0 is given by the relation $H_0=(H/M)\hbar\omega G^{1/2}$, where (H/M) is the ratio of the half-linewidth to the second moment, M, of the absorption band while G corresponds to the electron–phonon coupling strength. The Stokes shift between absorption and emission in the solid is related to G via $\Delta E_s=2\hbar\omega G$. Ophir's experimental data[23] for $H(T)$ in Xe/Ar(s) yield $\omega=63$ cm^{-1}, $H_0=660$ cm^{-1}, $H/M=2.00\pm 0.05$ (temperature independent) and $G=26$. The large electron–phonon coupling is responsible for the large Stokes shift. From the absorption data the Stokes shift is estimated to be $\Delta E_s=0.5$ eV, in reasonable agreement with the direct emission results ($\Delta E_s=0.72$ eV).

(c) From the point of view of the tight binding approximation one should notice the surprisingly small environmental shift exhibited by the dense medium (solid and liquid Ar) on the position of the Xe $^3P_1 \rightarrow {}^1S_0$ emission. Absorption studies of the $^1S_0 \rightarrow {}^3P_1$ transition reveal large blue spectral shifts [i.e., +0.36 eV for Xe/Ar(l) and +0.68 eV for Xe/Ar(s)] which can be blamed on overlap orthogonality corrections. On the other hand, the emission bands corresponding to this transition [1490 ± 10 Å for Xe/Ar(l) and 1480 ± 10 Å for Xe/Ar(s)] are very close to the gas phase transition energy 1469 Å (the matrix-gas shift for emission being $\sim$0.05 eV).[24]

The large Stokes shifts for the lowest extravalence excitation of atomic impurities in solid and in liquid argon, bring the emission bands in the dense medium very close to the gas phase transition energies. Thus on the time scale of the radiative decay of the impurity atoms or molecules (10^{-9} sec for Xe impurity) the system exhibits the presence of practically unperturbed electronically excited Xe atoms in the dense media. These results can be adequately interpreted in terms of appreciable medium relaxation, resulting in the formation of a microscopic void (or "cavity") surrounding the excited state. It is now well established that the absorption spectra of atomic and molecular impurities in rare gas solids exhibit a large blue spectral shift[1,8] of the lowest intermediate type excitation in the solid relative to the lowest extravalence excitation in the gas phase. Adopting for a moment the description based on the tight binding scheme[6,7] we assert that the energy shift in the dense medium originates from the dominating role of nonorthogonality overlap corrections. Thus for the ground state nuclear configuration of the system, the charge distribution in the lowest extravalence excitation of the atomic or of the molecular impurity will strongly overlap the first coordination layer of the surrounding medium. We conclude that in the electronically excited state a local medium dilation will result in a relaxed state of the total system, which is characterized by a lower energy than the Franck–Condon "vertical" configuration initially excited from the ground electronic state. The stable configuration of the electronically excited impurity state is achieved by a balance between short range electron–medium repulsions and the medium rearrangement energy involved in the creation of a microscopic void surrounding the impurity. The physical situation is analogous to the formation of the electron bubble in liquid and solid He[26] and to the formation of positronium bubbles in liquid rare gases.[27] Recent studies of optical excitation and of emission between two electronically excited Rydberg states (i.e., the He 2^3P–2^3S transition and the He_2^* $a\,^3\Sigma_u^*$–$c\,^3\Sigma_g^+$ transition) in liquid He were interpreted in terms of a cavity surrounding the electronically excited species.[28]

There is one important qualitative difference between the cavity surrounding an electronic excitation and the electron bubble in dense media. The total energy of the electron bubble, $E_t^e(R)$, consists of an electron kinetic energy, $KE(R)$, term, an electron–medium (repulsive) interaction term, $PE^e(R)$, and the medium rearrangement energy, $E_M(R)$, so that $E_t^e(R)=KE(R)+PE^e(R)+E_M(R)$, where R represents a radial displacement.[26] On the other hand, the total energy for the excited impurity state is $E_t^i(R)=E^0+PE^i(R)+E_M(R)$, where E^0 is the "free" impurity atom electronic excitation energy while $PE^i(R)$ represents the impurity–medium (repulsive) interaction energy. It is important to note that the $KE(R)$ term does not appear in $E_t^i(R)$. Thus in the case of the electron or positronium bubbles a large (on the scale of interatomic spacings) bubble has to be formed to compensate for the increased kinetic energy of the trapped electron or positronium. On the other hand, the medium dilation surrounding an impurity excited state have just to decrease the $PE^i(R)$ term, whereupon the medium displacements in this case will be of the order of the interatomic spacings in the dense medium. Thus such a medium relaxation around an excited impurity can occur both in liquid and in solid rare gases, while in view of the large $E_M(R)$ term in a solid, electron or positronium "bubbles" do not form in solid rare gases (except in the unique case of solid He).[26d]

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