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Evidence of the existence of exciton states in liquid argon and exciton-enhanced ionization from xenon doping

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Experimental investigations have been performed on the ionization yield in rare-gas-doped liquid Ar excited by ^{207}Bi conversion electrons. The enhanced ionizaiton yield (13% relative to the ionization yield in pure liquid Ar) is observed for Xe-doped (1.6%) liquid Ar and is attributed to the ionizing excitation transfer process from Ar excitons to doped Xe. The saturated value of the enhanced ionization is in good agreement with the theoretical value obtained under the assumption that the same electron band structure and the same exciton states as those in solid Ar exist in the liquid, too. This provides strong evidence for the existence of the exciton states in liquid Ar. No significant increase in ionization is observed with Kr-doped liquid Ar. The relaxation processes in liquid Ar are discussed.

I. INTRODUCTION

In 1962, Baldini[1] observed exciton states in solid Ar, Kr, and Xe, and estimated the band-gap energies. He also observed trapped excitons in dilute rare gas alloys.[2] After that, Rice and Jortner,[3] and Raz and Jortner[4] suggested the existence of Wannier exciton states in liquid Ar, Kr, and Xe on the basis of their experimental results. Also, Beaglehole[5] obtained the exciton spectrum in liquid Xe which is very similar to that of solid Xe just below the melting point.

In 1969, one of the authors (T. D.) predicted[6] that the average energies, W values, expanded per electron-hole pair in liquid Ar, Kr, and Xe are smaller than those in the gaseous state, assuming that the conduction band exists in these rare-gas liquids as well as in the solid state. In order to confirm this prediction, Takahashi, Konno, and Doke[7] measured the W values for liquid Ar, Kr, and Xe using the steady-conduction-current method. The accuracy of W values obtained in this way was not high, but the results showed the same trend as that predicted by Doke. Recently, we have made a more precise measurement of W values in liquid Ar and Xe by the electron-pulse method[8,9] and confirmed that W values are clearly smaller than those in gaseous Ar and Xe. Such a reduction of W value in the liquid state was quantitatively explained by assuming that, as in the solid, a conduction band and exciton states exist even in the liquid (the detail of the theory is described in Ref. 8).

Baldini[2] estimated the lowest energy required to ionize Xe in solid Ar to be 10.5 eV, which is lower than the energy of excitons in solid Ar [12.0 eV for the $n=1$ ($^2P_{3/2}$) exciton]. Photoemission from Xe in solid Ar, which was observed by Ophir *et al.*[10,11] very recently, was interpreted as the ionization of Xe owing to electronic energy transfer from exciton states of liquid Ar, which are formed by ultraviolet photons. If this is so and the electronic band structure and the exciton states in liquid Ar are almost the same as those in solid Ar, then enhanced ionization may be observed in Xe-doped liquid Ar. This is very similar to the Jesse effect[12] in the gas phase, which is observed in He or Ne gas containing a very small quantity of a second gas whose ionization potential is lower than the first excited state of He or Ne.

Here, we consider first the excitation of the solid state by ionizing particles. In the optical approximation, the probability of producing an excited state of excitation energy E by ionizing particles is proportional to $f(E)/E$,[13] where $f(E)$ is the oscillator strength. The ratio of the number of excitons to electron-hole pairs N_{ex}/N_i is estimated to be 0.21 from $f(E)$ for solid Ar measured by the DESY group.[14] From this value we can estimate the exciton-enhanced ionization yield from Xe relative to pure Ar to be 0.21 at the maximum, where all excitons produced by ionizing particles ionize Xe.

Next, we consider the liquid state. The ionization potential of Xe is 10.58 eV in liquid Ar.[4] If we assume the existence of excitons in liquid Ar and that the electronic structure of the liquid is almost the same as that of the solid, then N_{ex}/N_i for liquid Ar is expected to be also 0.21. And if the additional ionization yield in Xe-doped liquid Ar is observed to be 0.21 relative to liquid Ar, this increase should be attributed to the exciton-enhanced ionization. The present experiment shows that this is the case. In addition to the experiment on Xe-doped liquid Ar, the measurement of ionization yield in Kr-doped liquid Ar was made. These results provide the same information on the exciton dynamics in the bulk state as that obtained by Ophir *et al.*[10,11]

II. EXPERIMENTAL PROCEDURE

To observe the electron pulses, a gridded ionization chamber was used. The collector and the cathode, 17 mm in diameter, are made of stainless steel. The grid is an array of wires of 10-μm diameter strung with a 100-μm spacing onto a square flange. The distance between the cathode and the grid is 3.8 mm, and 1.8 mm between the grid and the collector. Electron pulses produced by ^{207}Bi conversion electrons were measured by an amplifier with 1-μsec differential and 1-μsec integral time constants. The chamber was fixed with three feed-through seals in a stainless-steel vessel. The chamber and the gas filling system were baked at about 100 °C for more than 24 h. The ultimate vacuum obtained was about 3×10^{-7} Torr.

High purity Ar and Xe gases (obtained from Toshiba Co., Ltd.) were fed into a barium-titanium getter purifier having a volume of 18 liters in order to mix. Then the purifier was operated at about 600 °C. The gas mixture was condensed at a pressure of about 2 atm into the vessel which was immersed in a refrigerant of 1 : 9 liquid-nitrogen–oxygen mixture. It took about 30 min to condense a gas mixture of about 80 liter atm; after condensation, the refrigerant was replaced by liquid oxygen.

The measurements were made at a pressure of 2–3 atm. The Xe concentration in the liquid was assumed to be equal to that of the composition of the gas mixture. Any detectable change in the enhanced ionization yield for Xe-doped liquid Ar was not observed at the relatively high pressure of about 5 atm. This fact seems to show that the aggregation of Xe is not serious in our experiment.

III. EXPERIMENTAL RESULTS

Figure 1 shows a typical pulse-height spectrum of ^{207}Bi conversion electrons with and without Xe. The 0.976-MeV peak with Xe is clearly higher than that for pure liquid Ar; reproducible results were obtained for different experimental runs.

Figure 2(a) shows the saturation curves for the 0.976-MeV peak. The error of measurement at each point in the figure is estimated to be about 0.5%. As seen from the figure, the saturation of these curves is not complete even at the maximum electric field. Typically, the pulse height (V) increased by about 1.5% while the field (E) was varied from 14 to 17 kV/cm and extrapolation ($1/E$-$1/V$ plot) was made to evaluate the saturation value V_{ext}. This extrapolation is based on the Jaffe theory.[15] Although the theory describes the recombination of two massive ions, not that of electrons and ions, it is often used to evaluate the saturation values.[7,16,17]

Here, we use V_{ext} as well as the pulse height at 17 kV/cm, V_m, as a measure of the ionization yield. Figure 2(b) shows the variations of relative ionization yields $(V_{ext})_{Ar+Xe}/(V_{ext})_{Ar}$ and $(V_m)_{Ar+Xe}/(V_m)_{Ar}$ with the Xe concentration C(Xe) in liquid Ar. The discrepancy between them is less than 0.8% over all the range of C(Xe). The measured enhanced ionization yield increases rapidly with C(Xe) and then more slowly, approaching finally to a saturation value.

Estimation of the direct ionization yield for Xe doping I_d(Xe) by ^{207}Bi conversion electrons and its secondary electrons is made approximately by using the formula[18]

$$I_d(\mathrm{Xe}) = [I(\mathrm{Xe})/I(\mathrm{Ar}) - 1]\,SC(\mathrm{Xe})I(\mathrm{Ar}) \ , \qquad (1)$$

where I(Ar), I(Xe) are the ionization yields for liquid Ar and liquid Xe, respectively, and S is the ratio for the average stopping powers for Ar and Xe. By using the value of $I(\mathrm{Xe})/I(\mathrm{Ar}) = 23.6/15.6$,[8,9] and $S = 1.91$,[18] $I_d(\mathrm{Xe})/I(\mathrm{Ar})$ is estimated to be 0.016 for the highest C(Xe) of 1.6%. This value shows that I_d(Xe) is much smaller than the enhanced ionization yield.

We also measured the ionization yield for Kr-doped liquid Ar. The increase relative to I(Ar) was observed to be 0.015 ± 0.002 for 4.6% Kr doping in liquid Ar. Any detectable increase in the ionization was not observed for $C(\mathrm{Kr}) \leq 1.6\%$. The direct ionization of Kr was also calculated from Eq. (1) to be about 0.01 at $C(\mathrm{Kr}) = 4.6\%$. Here, we used $I(\mathrm{Kr})/I(\mathrm{Ar}) = 23.6/20.5$ (Refs. 7 and 8) and $S = 1.37$.[18] The increase rate of the ionization yield for Kr is very slow compared with that for Xe.

IV. DISCUSSION

Enhanced ionization has been observed in Xe-doped liquid Ar but no significant increase was observed in Kr-doped liquid Ar. In order to explain these experimental facts we assume that the electronic structure in liquid Ar and rare-gas-doped liquid Ar are almost the same as those of the corresponding solids. This assumption, which has

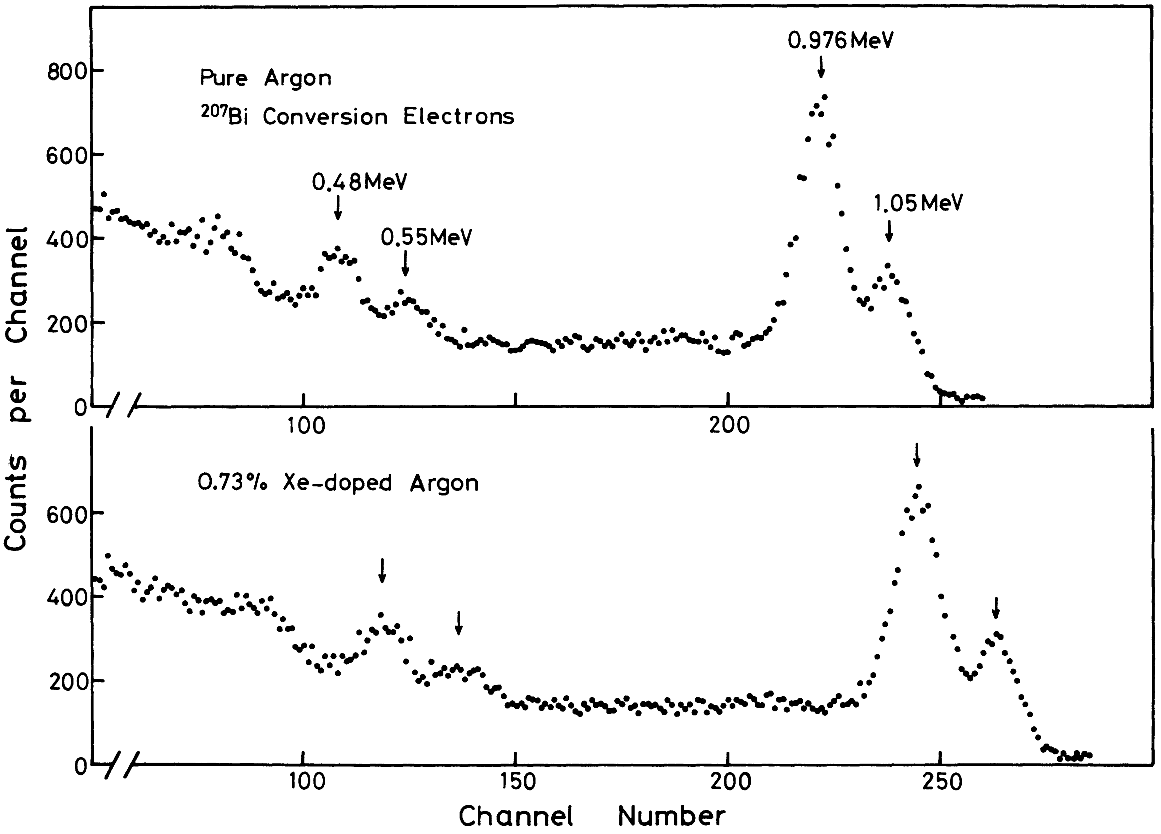

FIG. 1. Pulse-height spectrum of ^{207}Bi conversion electrons measured with the liquid-Ar ionization chamber with and without Xe at the electric field of 13.7 kV/cm.

already been used in Ref. 8, is justified in the following discussion.

According to this assumption the ionization potential of Kr and the excitation energies of $n=1(^2P_{3/2})$ and $n=1(^2P_{1/2})$ states in liquid Ar are 12.5,[11] 12.0, and[1] 12.3 eV, respectively. Therefore, Kr can not be ionized by $n=1$ excitons in liquid Ar.

The vacuum ultraviolet luminescence spectrum of solid Ar is attributed to the emission from excited dimers, Ar_2^*, i.e., self-trapped excitons.[19] The luminescence spectrum of liquid Ar is very similar to that of solid Ar.[20] This fact supports the assumption that the excitons are deexcited and Ar_2^* are formed in liquid Ar. Since the electronic excitation energy of Ar_2^* is lower than the ionization potential of Xe, Xe dopant is not ionized by Ar_2^*.

In solid Ar, the transition of excitons from higher excited states to $n=1$ states occurs due to multiphonon radiationless relaxation processes. However, the relaxation time of the multiphonon relaxation process is not yet known. If the relaxation time is fast, we can expect that all the ionizing energy transfer to the doped rare gas occurs from the lowest $n=1(^2P_{3/2})$ and $n=1(^2P_{1/2})$ states. If this is the case, the enhanced ionization will not be observed in Kr-doped liquid Ar. Our experimental result supports the above interpretation.

The enhanced ionization in Xe-doped liquid Ar is attributed to the ionizing excitation energy transfer from Ar excitons to Xe doping. By considering the ionizing excitation energy transfer and self-trapping processes in Xe-doped liquid Ar, the enhanced ionization yield I_{enh} is given relative to $I(\text{Ar})$ as follows:

$$I_{\text{enh}}/I(\text{Ar}) = (N_{\text{ex}}/N_i)\{k\tau n(\text{Xe})/[1+k\tau n(\text{Xe})]\}, \quad (2)$$

where $kn(\text{Xe})$ is the rate constant for the ionization of Xe, $n(\text{Xe})$ the number density of Xe in liquid Ar and τ the relaxation time of $n=1$ excitons for self-trapping.

The values of N_{ex}/N_i and $k\tau$ were evaluated from the data of Fig. 2(b) by the least-squares fitting to Eq. (2); the values obtained are shown in Table I.

In the above analysis, we neglected the contribution to the ionization of Xe due to subexcitation electrons. This contribution relative to $I(\text{Ar})$ is estimated to be about 0.02 by using the energy distribution of subexcitation electrons for the gas

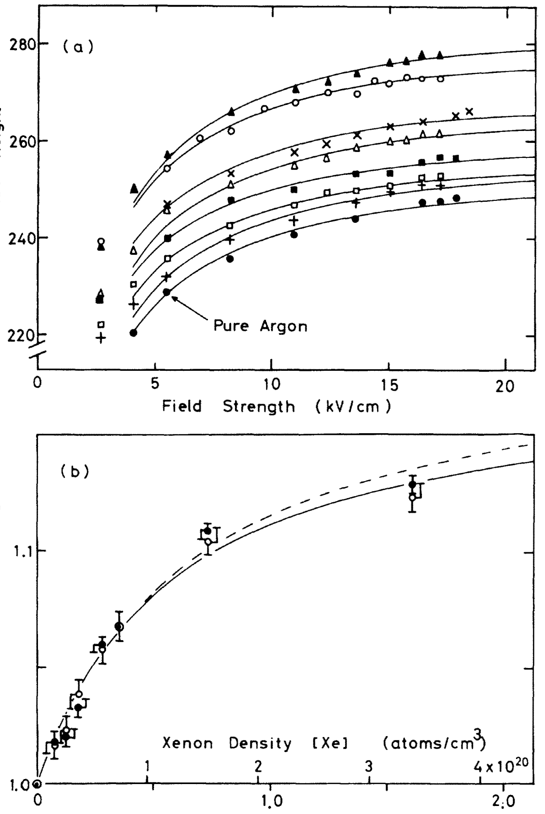

FIG. 2. (a) Saturation curves of ionization for 0.976-MeV conversion electrons for various concentration of Xe. The symbols ● + □ ■ △ × ○ ▲ represent pure Ar, 0.08, 0.12, 0.18, 0.28, 0.37, 0.73 and 1.6 at.% Xe concentration, respectively. The smooth curves are calculated by the $1/E$-vs-$1/V$ plot as described in the text. (b) Relative ionization yield as a function of Xe concentration for the saturation value V_{ext} (●) and for the pulse height at 17 kV/cm, V_m, (○). The smooth and dotted curves are calculated by the least-squares fitting to Eq. (2) for V_{ext} and V_m, respectively. The discrepancy between the evaluated N_{ex}/N_i by the least-squares fitting to Eq. (2) from V_{ext} and that from V_m is 5% and is within the estimate error.

phase estimated by Platzman,[21] and the excitation[22] and ionization[23] cross sections for Xe atom by electrons.

The ratio of N_{ex}/N_i for solid Ar was calculated to be 0.21 (Table I) by assuming that all the excitons which lie above the bottom of the conduction band dissociate to electron-hole pairs immediately. As shown in Table I, the agreement between the experimental value of N_{ex}/N_i in liquid Ar and the theoretical value in the solid is good. This agreement supports an approach on the basis of the assumption that liquid Ar has almost the same electronic structure as that in solid Ar.

Ophir *et al.*[11] obtained $k\tau = 4\times10^{-20}$ cm^3 from the concentration dependence of the photoemission yield from Xe-doped solid Ar.[24] Their value for the solid, which is also shown in Table I, is reliable to within a numerical factor of 2 as described in their previous paper.[10] Table I shows that the $k\tau$ value for the liquid is a factor of 6 lower than that for the solid.

In our experiment, we considered that the Xe concentration in liquid Ar is equal to that of the composition of the gas mixture. Raz and Jortner reported[4] that aggregation of Xe occurs when the gas mixture was liquified. The aggregation effect will make the concentration of atomic Xe in liquid Ar lower than that of the gas mixture. If this were the case, the measured $k\tau$ value might be lower than the actual one.

The $k\tau$ value of Ophir *et al.* was obtained for a thin solid layer. On the other hand, the $k\tau$ value obtained in our experiment is that for the bulk. From the discussions above, it seems premature, at the present time, to discuss the reason for the difference between the $k\tau$ values in liquid and solid phases.

The number of excitons with excitation energy higher than the ionization potential of Kr (12.5 eV) is estimated to be 0.07 relative to N_i in the optical approximation by using $f(E)$ for solid Ar.[14] The enhanced ionization yield at $C(\mathrm{Kr}) = 4.6\%$ is observed to be 0.005 ± 0.002 relative to $I(\mathrm{Ar})$, by subtracting $I_d(\mathrm{Kr})$. Since Kr dopant is not ionized by $n=1$ excitons, the enhanced ionization yield is determined by the two competing processes: the ionizing excitation energy transfer process from $n\geq 2$ excitons to Kr with the rate constant of $k'n(\mathrm{Kr})$, and the multiphonon radiationless relaxation process of $n\geq 2$ excitons with the relaxation time of τ'. By substituting $I_{enh}/I(\mathrm{Ar}) = 0.005 \pm 0.002$, $N_{ex}/N_i = 0.07$ to Eq. (2), in which $kn(\mathrm{Xe})$ and τ are replaced by $k'n(\mathrm{Kr})$ and τ', we obtain $k'\tau' = (7\pm3)\times10^{-23}$ cm^3.

Here, k and k' are interpreted as σv and $\sigma' v'$, respectively, where σ and σ' are the ionizing excitation energy transfer cross sections from $n=1$ states to Xe doping and from $n\geq 2$ excitons to Kr doping, and v, v' are the exciton group velocities for these states. The ratio σ/σ' is estimated to be about 2 to 3 from the theoretical cross sections for the Penning process in gas phase calculated by Watanabe and Katsuura,[25] and the ratio v/v' is

TABLE I. N_{ex}/N_i and $k\tau$ for Xe-doped liquid and solid Ar.

	N_{ex}/N_i	$k\tau$ (10^{-21} cm^3)
Liquid Ar (this expt.)	0.19 ± 0.02	7.2 ± 0.8
Solid Ar	0.21[a]	40[b]

[a] Theory, see the text.

[b] Reference 10.

about one. Therefore, we can estimate that the relaxation of excitons in $n \geq 2$ states due to the multiphonon radiationless process is several tens times faster than the relaxation time of $n = 1$ excitons forming Ar_2^*.

V. CONCLUSIONS

From the experiments on ionization yield in Xe-doped and in Kr-doped liquid Ar excited by ^{207}Bi conversion electrons, the following conclusions were drawn: (i) Enhanced ionization was observed from Xe doping owing to electronic energy transfer from exciton states of liquid Ar, directly demonstrating the existence of the exciton states in liquid Ar. (ii) No significant enhanced ionization was observed from Kr doping. This supports the belief that the multiphonon radiationless relaxation process of $n \geq 2$ excitons to the lowest $n = 1(^2P_{3/2})$ and $n = 1(^2P_{1/2})$ states is very fast and that the ionizing excitation energy transfer process occurs from the lowest $n = 1$ exciton states of liquid Ar.

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