



# Radiation-induced formation of stable charge centers in rare-gas solids

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## Abstract

Molecular ion centers (XeAr)<sup>+</sup> in solid Ne were produced by deposition of an ion-containing gas on a cooled substrate. Laser-induced fluorescence (LIF) and excitation yield were studied in the range of transitions between the ground state of the ionic centers and the lower excited states related to the <sup>2</sup>P<sub>1/2</sub>, <sup>2</sup>P<sub>3/2</sub> limits of Xe<sup>+</sup>. The fluorescence of (XeAr)<sup>+</sup> exhibits a vibrational structure with a spacing between the peaks of the fluorescence progression of about  $\omega_e = 11.1$  meV. © 2000 Elsevier Science B.V. All rights reserved.

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## 1. Introduction

Charge carriers in insulators, their stability and dynamics are a topic of considerable importance in radiation physics, material science and chemistry. The study of the problem in rare-gas solids (RGS) – the widest band gap insulators – has an advantage because the lattice rearrangement induced by phonon interaction with electronic excitation is not obscured by interatomic interaction which is

extremely weak in these solids. The formation of ionic centers in RGS is closely related to the fundamental problem of hole self-trapping [1], and is of special interest in view of the prominent role of holes in radiation-induced phenomena, charge transport, dosimetry and photochemistry in cryogenic solids. Charge centers in RGS were tested by the thermoluminescence method [2–4]. A new experimental approach [5] to study ionic centers was employed: the investigation of ‘frozen plasma’. The samples were grown from discharge so that the ionic species were embedded into the growing matrix. It was found [6] that the configuration and the electronic structure of intrinsic ionic centers are identical with those of self-trapped holes, which were generated in situ with vacuum ultraviolet ionizing radiation. The intrinsic ionic centers

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have been shown to be ionic dimers. To get more knowledge about the formation of ionic dimer centers in the lattice we concentrate on the study of heteronuclear centers in the lattice. The present paper deals with  $(\text{XeAr})^+$  in a neon matrix. The spectroscopic study at selective excitation was performed in the range of the electronic transitions between the ground state and the lower excited states arising from the limits  $\text{Rg}(^1S) + \text{Rg}^+(^2P_{1/2,3/2})$ .

## 2. Experiment

The samples were grown by deposition of ion-containing gas from a pulsed supersonic jet source [7]. High-purity gases (Ne and Ar 99.9990%, Xe 99.998%) were used to make the mixture. The samples were premixed by standard gas-handling technique. The experimental chamber and gas inlet system were degassed by heating in vacuum before the experiments. The pressure in the deposition chamber was  $6 \times 10^{-8}$  mbar. The concentration of Xe and Ar was kept low enough to give a preference to heteronuclear center formation. The mixture of Xe:Ar:Ne (1:1:300) was discharged using two electrodes kept at up to 1.5 kV. The ionic composition of the jet was controlled with a quadrupole mass spectrometer to make sure that only atomic ions are embedded into the matrix. Then molecular ionic centers were formed via coupling of an  $\text{Rg}^+$  ion with a neutral Rg atom from the surroundings. In addition,  $\text{Xe}^+$  and  $\text{Ar}^+$  centers were generated in the matrix under irradiation by vacuum ultraviolet (VUV) light from the discharge in Ne. Because resonant transitions of Ne atoms in the gas (16.848 and 16.671 eV) are shifted towards lower energy with respect to the edge of the intrinsic absorption of the matrix (17.1 eV), this VUV radiation efficiently penetrated through the whole matrix. Ionic species were accumulated over many pulses. Each pulse of about 50 nmol deposits about 20 monolayers on a metal substrate. The total time to grow the sample was about 1000 s. The sample was finally 10  $\mu\text{m}$  thick. The amount of deposited gas was determined by observing the gas pressure decrease in a known volume and interferometrically. Producing the

ions just one microsecond before supersonic expansion has the advantage of minimizing the wall-induced recombination of ions in the discharge unit. To minimize the recombination of charged centers in the solid, the deposition temperature  $T_d = 7$  K was kept below the temperature of the main thermoluminescence peaks from solid Ne measured at  $T_{\text{TL}} = 10$  and 12.5 K.

After deposition, we rotated the sample by  $90^\circ$  for the spectroscopic studies. A modified Bruker 120 IFS HR spectrometer was used to characterize the samples. The presence of impurities and defects was monitored by the measurement of the infrared absorption spectra and analysis of the base line. The following characteristic impurity bands measured in a neon matrix [8,9] were used for the control:  $\text{H}_2\text{O} - 1631 \text{ cm}^{-1}$ ;  $\text{CO}_2 - 2338.7 \text{ cm}^{-1}$ ;  $\text{CO} - 2140.9 \text{ cm}^{-1}$ . The residual gas contamination was smaller than  $10^{-4}$ . The laser-induced fluorescence (LIF) study and the measurement of the excitation spectrum were performed with a Ti-Sapphire tunable laser pumped by a Coherent argon ion laser Innova 200. The time needed for data acquisition was 1000 s at  $0.5 \text{ cm}^{-1}$  resolution. The excitation spectrum was recorded by monitoring the integral intensity of the LIF band using a GaAs optical filter (cut-off edge at 1.376 eV) and an  $\text{LN}_2$ -cooled germanium detector.

## 3. Results and discussion

Charge centers generated from discharge as well as in situ manifest themselves in the matrix as species of opposite charge. In order to be stabilized in the lattice, the charge centers have to be spatially separated and immobile. Positively charged ionic centers can be stabilized in the lattice by the presence of electron traps – shallow traps like lattice defects and deep ones (impurities with high electron affinity). As long as the temperature is low enough, the charge carriers are immobile, the ionic centers remain stable and can therefore be studied.

The LIF spectra taken from the triple mixture of Xe, Ar and Ne (1:1:300) exhibit a pronounced near-infrared emission band centered at 1.338 eV with a full width at half the maximum (FWHM) of

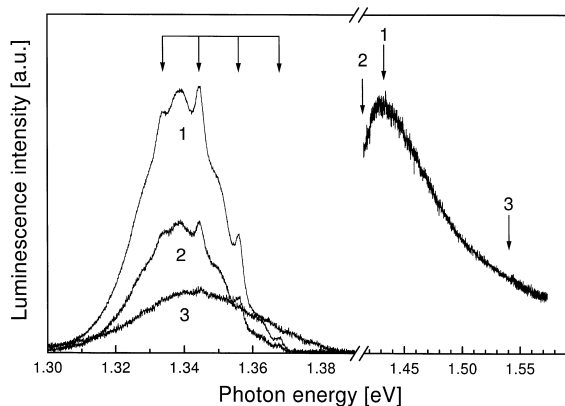


Fig. 1. Laser-induced fluorescence spectra (left-hand side) and excitation spectrum (right-hand side) of a mixture Xe:Ar:Ne (1:1:300) deposited at 7 K. The arrows at the right-hand side mark the excitation energies of the corresponding LIF spectra.

26 meV. A typical LIF band at different wavelengths of excitation is shown in Fig. 1. The corresponding excitation energies are marked by the arrows at the right-hand panel of the figure. In the high-resolution scans ( $\Delta\nu = 0.5 \text{ cm}^{-1}$ ) we found that the band is structured with a spacing between the peaks of the fluorescence progression of about 11.2 meV. In order to assign this band we measured an excitation spectrum of this emission, which is reproduced in Fig. 1. Unlike the LIF spectrum, the excitation curve is structureless with FWHM estimated to be 77 meV. In order to be sure that the centers of the observed emission involves Xe and Ar atoms, we measured the LIF spectra from a mixture containing only one dopant and deposited from discharge under identical conditions. No sign of the considered emission was observed.

The most reasonable candidate for the emitting state is the  $2(1/2)$  state of the  $(\text{XeAr})^+$  center. This state has a minimum of about  $D_e = 0.064 \text{ eV}$  [10] and the transition to the ground state  $1(1/2)$  is dipole-allowed. These states converge to the  $^2P_{1/2}$ ,  $^2P_{3/2}$  limits of  $\text{Xe}^+$  split by spin-orbit coupling of 1.31 eV. Based on the computed potentials [10] the energy of the transition  $1(1/2) \rightarrow 2(1/2)$  in an absorption (excitation) spectrum is expected to be around 1.41 eV at an interatomic distance  $R_e$  of 6.2 a.u. This is fairly close to the maximum of the

excitation spectrum at 1.43 eV. The minimum of the excited state is shifted towards a larger  $R_e = 6.8 \text{ a.u.}$  [10]. The emission following the relaxation to the  $v' = 0$  level of the excited state is estimated to be centered near 1.35 eV. This again is close to the maximum of the LIF band at 1.338 eV. The fact that there is a good correspondence between the experimental data and the data of the theoretical calculations supports the model of a charge-induced dipole with a charge localized at the Xe atom. Indeed the computations [10] were performed for the case of the  $(\text{XeAr})^+$  in the gas phase and one can expect a matrix effect. This assignment is supported by the recent results of Peterson and Gürtler [11]. The maximum of the LIF band excited by near infrared light in our experiments is fairly close to the band observed under ionization of the triple mixture Xe, Ar and Ne with VUV light from a synchrotron [11]. The excitation spectrum of the emission at 1.33 eV measured in the VUV range provides evidence that the centers of the considered emission involve  $\text{Xe}^+$  ions and neutral Ar atoms. The observation of the LIF 28 h after deposition from discharge demonstrates the stability of these charge centers at low temperatures.

It is interesting to discuss the structure of the LIF band found in our experiments. The spacing between the peaks of the fluorescence progression is close to  $\omega_e = 11.1 \text{ meV}$  of the ground state  $(\text{XeAr})^+$  observed in the gas phase [12]. Taking into account that major differences in the solvation geometry of the  $1(1/2)$  and  $2(1/2)$  states is not to be expected, it is not surprising that one observes zero-phonon lines in the LIF spectrum. The high-energy peak at the LIF band (1.368 eV) can then be tentatively assigned to the  $0 \rightarrow 0$  origin of the electronic transition  $2(1/2) \rightarrow 1(1/2)$ . The absence of zero-phonon lines and a resolvable vibrational structure from the excitation spectrum is very likely to be due to smaller vibrational spacing in the shallow upper-state potential and very fast vibrational relaxation. The observation that the excitation profile extrapolates roughly to the energy of the first observed emission band suggests that it steams from the  $0 \rightarrow 0$  transition. This numbering could be confirmed by an experiment with  $^{36}\text{Ar}$ .

#### 4. Conclusion

The spectroscopic study of molecular ions  $(\text{XeAr})^+$  in solid Ne is presented. The centers were formed in the lattice via coupling of  $\text{Xe}^+$  ions introduced into the solid with nearby Ar atoms. Upon excitation by a Ti-Sapphire laser the LIF of these ions was observed. Based on the measured excitation yield in the near-infrared range and the comparison with computed data [10] as well as the excitation yield of the emission in the VUV range [11], the LIF band is assigned to the dipole-allowed transition  $1(1/2) \rightarrow 2(1/2)$  of  $(\text{XeAr})^+$  in the Ne matrix. The structure of the LIF band was detected for the first time.

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