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Neutral and charged excimer complexes in cathodoluminescence spectra from substrate-free icosahedral and crystalline clusters of argon

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We studied cathodoluminescence spectra from substrate-free argon clusters produced in a supersonic jet expanding adiabatically into a vacuum. The average cluster size varied from 500 to 8900 atoms per cluster. As clusters grew bigger, their structure changed from a quasicrystalline icosahedral structure with a 5-fold symmetry axis to a crystalline fcc one. Clusters were excited by a 1-keV electron beam. Luminescence spectra were measured in the 8.1-11.8 eV energy range containing emission bands of the neutral and charged excimer complexes $(Ar_2)^*$ and $(Ar_4^+)^*$. An analysis of the intensity of radiation from their relaxed vibrational states was performed on the basis of a new approach that allows us to take into account the fraction of jet substance condensed into clusters. It was shown that in crystalline clusters with an fcc structure the emission from neutral $(Ar_2)^*$ molecules comes from within the bulk of a cluster, while the radiation from charged $(Ar_4^+)^*$ complexes originates in its near-surface layers. We found the cluster size range in which the jet is dominated by quasicrystalline clusters with the structure of multilayer icosahedron and demonstrated that the transition from icosahedral clusters to fcc clusters occurs when the average cluster size is 1400±400 atoms.

Keywords: argon cluster, cathodoluminescence spectrum, icosahedral structure, fcc structure

В работе исследованы спектры катодолюминесценции свободных кластеров аргона, формирующихся в сверхзвуковой струе, адиабатически расширяющейся в вакуум. Средний размер кластеров варьировался от 500 до 8900 атомов на кластер, при этом их структура изменялась с увеличением размера кластера от квазикристаллической с осью симметрии 5-го порядка до кристаллической гцк структуры. Кластеры возбуждались электронным пучком с энергией 1 кэВ. Регистрация спектров люминесценции проводилась в области свечения нейтральных и заряженных эксимерных комплексов $(Ar_2)^*$ и $(Ar_4^+)^*$, 8,1-11,8 эВ. В рамках нового подхода, позволяющего учесть долю сконденсированного в кластеры вещества в струе, проведен анализ интенсивностей излучения из колебательно-релаксированных состояний $(Ar_2)^*$ и $(Ar_4^+)^*$. Установлено, что в кристаллических кластерах с гцк структурой свечение нейтральных молекул $(Ar_2)^*$ происходит из всего объема кластера, в то время как заряженные комплексы $(Ar_4^+)^*$ излучают из приповерхностного слоя. Выделена область размеров, при которых в струе преобладают квазикристаллические кластеры со структурой многослойного икосаэдра, и показано, что переход от икосаэдрических кластеров к кластерам с гцк структурой происходит при среднем размере кластеров в струе 1400±400 ат/кл.

Ключевые слова: кластер аргона, спектр катодолюминесценции, икосаэдрическая структура, ГЦК структура

У роботі досліджено спектри катодолюмінесценції вільних кластерів аргону, що формуються в надзвуковому струмені, який адіабатично розширюється у вакуум. Середній розмір кластерів варіювався від 500 до 8900 атомів на кластер, при цьому їхня структура змінювалася зі збільшенням розміру кластера від квазикристалічної з віссю симетрії 5-го порядку до кристалічної ГЦК структури. Кластери збуджувалися електронним пучком з енергією 1 кеВ. Реєстрація спектрів люмінесценції здійснювалася в області світіння нейтральних та заряджених ексимерних комплексів $(Ar_2)^*$ і $(Ar_4^+)^*$, 8,1-11,8 еВ. У рамках нового підходу, який дає змогу врахувати долю сконденсованої в кластери речовини у струмені, проведено аналіз інтенсивностей випромінювання з коливально-релаксованих станів $(Ar_2)^*$ і $(Ar_4^+)^*$. Установлено, що в кристалічних кластерах з ГЦК структурою світіння нейтральних молекул $(Ar_2)^*$ відбувається з усього об'єму кластера, у той час як заряджені комплекси $(Ar_4^+)^*$ випромінюють з приповерхневого шару. Виділено область розмірів, при яких у струмені переважають квазикристалічні кластери зі структурою багатошарового ікосаедра, і показано, що перехід от ікосаедричних кластерів до кластерів з ГЦК структурою відбувається за середнього розміру кластерів у струмені 1400±400 ат/кл.

Ключові слова: кластер аргону, спектр катодолюмінесценції, ікосаедрична структура, ГЦК структура.

Introduction

Atomic and molecular clusters have been widely studied in such areas as physics, astrophysics, chemistry, medicine, materials science, etc. The fundamental interest in such systems is largely due to a number of unusual properties they display which are not observed in bulk samples. Among them is, for example, influence of cluster size on relaxation processes of electron excitations [1] and

on cluster structure [2].

One of the main methods for obtaining substrate-free clusters of various elements and compounds is condensation of a gas (gas mixture) in a supersonic jet exhausting into a vacuum. Luminescence studies of rare-gas clusters produced in supersonic jets (see, e.g., Refs. [3,4]) demonstrate that VUV spectra from clusters depend greatly on the jet composition and cluster size.

The purpose of the present paper is to find and study a dependence of integrated intensities of neutral and charged excimer complexes in cathodoluminescence spectra of argon clusters on the fraction of jet substance condensed into clusters.

Experimental

The paper presents the results of our cathodoluminescence study of substrate-free clusters of solid argon generated in the process of argon gas condensation in a supersonic jet which adiabatically expands through a conical nozzle into a vacuum. The cluster size and structure were varied by changing the gas temperature T_0 at the nozzle inlet, the stagnation pressure p_0 being constantly kept equal to 1 atm. The average cluster size in the jet was found by using a modified Hagena relation [5].

Medium-sized clusters were studied in the paper with average sizes and diameters varying in the range 500 to 8900 atoms per cluster (at/cl) and 32 to 87 Å, respectively. The cluster temperature amounted to about 40 K and did not depend on the parameters of gas at the nozzle inlet [6].

At a distance of 30 mm from the nozzle outlet, clusters were excited by a 1-keV electron beam. Their cathodoluminescence spectra were registered in the photon energy range of 8.1-11.8 eV, which contains emission bands of the neutral and charged excimer complexes $(Ar_2)^*$ and $(Ar_4^+)^*$. More experimental details can be found in Refs. [7,8].

Results and discussion

Cathodoluminescence spectra from clusters of all the sizes studied in the paper are shown in Fig. 1. Two examples of their decomposition into spectral components are presented in Fig. 2 for clusters with the average size $\overline{N} \approx 1000$ at/cl (cluster diameter being 42 Å) and 8900 at/cl (87 Å). The spectra consist of a few bands emitted from molecular and atomic states of argon. The narrow band at 11.61 eV corresponds to the $^3P_1 \rightarrow {}^1S_0$ transition in single atoms of argon desorbed from clusters after their excitation by electrons as well as in argon atoms still present in the gaseous fraction of the jet which did not condense into clusters. There are two pronounced molecular continua in the low-energy section of the spectra which are emitted from clusters: the band at 9.6 eV corresponds to transitions from vibrationally relaxed levels of neutral excimer

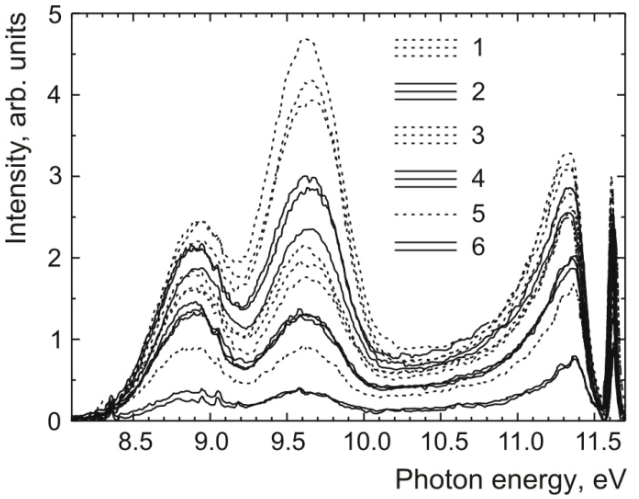

Fig. 1. Cathodoluminescence spectra from clusters with the following average sizes (at/cl): 8900 (1), 4500 (2), 2900 (3), 1800 (4), 1000 (5), 500 (6). Each cluster size is presented by one to three curves measured in different experimental cycles. The discrepancies among the curves corresponding to one and the same cluster size are due to experimental errors which affect the calculated cluster size values.

complexes $(Ar_2)^*$ in the states $^3P_1 + {}^1S_0$ and $^3P_2 + {}^1S_0$ (see., e.g., Ref. [9]), while the band at 8.9 eV can be assigned to transitions occurring in charged complexes $(Ar_4^+)^*$ [10,11]. In the higher-energy spectral range, we can see emission from partly vibrationally relaxed (W′ band at 10.6 eV) and vibrationally excited (asymmetric W band with a maximum at 11.3 eV) states of $(Ar_2)^*$ molecules in clusters. It should be noted that in bulk samples of solid argon the W band has

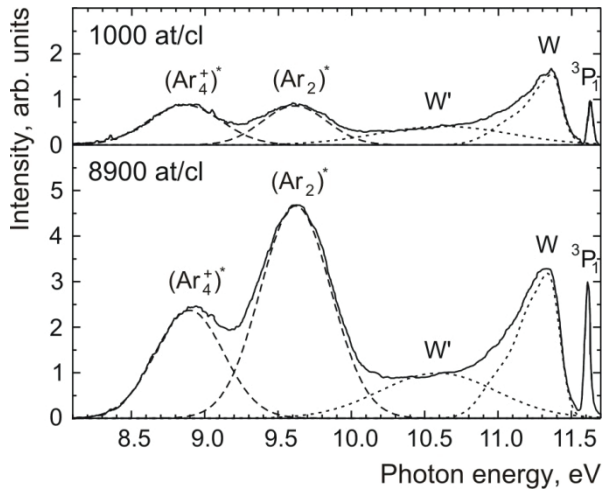

Fig. 2. Luminescence spectra from substrate-free argon clusters with the average sizes $\overline{N} \approx 1000$ and 8900 at/cl in the spectral regions of the $(Ar_2)^*$, $(Ar_4^+)^*$, W′, and W bands. Experimental data are shown as solid curves. Decomposition of the spectra into components is shown as dashed ($(Ar_2)^*$ and $(Ar_4^+)^*$) and dotted (W′ and W) curves.

a significantly lower relative intensity than it has in clusters [12,13]. Analysis of the W′ and W bands was only needed to fit more accurately the profiles of the molecular continua $(Ar_2)^*$ and $(Ar_4^+)^*$ which are of main interest to the present study.

Integrated intensity of the molecular continua $(Ar_2)^*$ and $(Ar_4^+)^*$ emitted from clusters depends on cluster excitation cross-section, number of clusters excited, and probability of relaxation of the created excitations through a radiative channel under study:

$$I \sim \sigma_{exc} n_{cl} W_{rad}, \quad (1)$$

where I is integrated intensity of an emission band, σ_{exc} is excitation cross-section for one cluster, n_{cl} is number of clusters excited, and W_{rad} is probability of radiation through the radiative channel which gives rise to the analyzed emission band.

The number of clusters n_{cl} excited in unit time is given by the total number of atoms n_0 passing through the excitation area in unit time, fraction of substance c_{cl} condensed into clusters, and average size $\bar{N}$ of clusters in the excitation area:

$$n_{cl} = c_{cl}\, n_0 / \bar{N}\,. \quad (2)$$

It was shown theoretically in Ref. [14] that the maximum concentration c_{max} of bound atoms at the end of expansion of pure atomic gas is:

$$c_{max} \sim \frac{T_*}{\varepsilon_0} \ln N_{max}, \quad (3)$$

where N_{max} is the maximum number of cluster atoms at the end of expansion, T_* is the condensation onset temperature, and ε_0 is the mean binding energy per cluster atom. In the case of large clusters, when the binding energy is weakly dependent on cluster size, being close to its value for a macroscopic system, the ratio $\frac{T_*}{\varepsilon_0}$ can be taken as constant.

Taking into account that in our experiments the jet excitation area was 30 mm away from the nozzle outlet, that is where clusters already possess the largest average size possible and the process of their further growth is thus ineffective, and assuming that the maximum cluster size N_{max} in the excitation area is proportional to the weight-average cluster size $\bar{N}$, we can conclude that the fraction of the substance c_{cl} condensed into clusters is given by Eq. (3) with a numerical factor under the logarithm:

$$n_{cl} \sim n_0 \ln \bar{N} / \bar{N} + A\, n_0 / \bar{N}\,, \quad (4)$$

where A is the logarithm of the numerical factor. Hence

$$n_{cl} \sim n_0 \ln \bar{N} / \bar{N} \quad (5)$$

under the assumption that the second term in Eq. (4) is small for clusters of the sizes studied in the paper. The value n_0 depends on the stagnation pressure p_0, which was constant in our experiments, so

$$n_{cl} \sim \ln \bar{N} / \bar{N}\,. \quad (6)$$

Cross-section of cluster excitation by an electron is, in the general case, a function of the electron energy and cluster size. In the case of clusters excited by electrons of the same energy, we can use the cluster geometrical cross-section, which is proportional to $\bar{N}^{2/3}$, as its excitation cross-section. Then Eq. (1) can be rewritten as follows:

$$I \sim \bar{N}^{2/3} n_{cl} W_{rad} \sim \bar{N}^{-1/3} \ln \bar{N}\, W_{rad}. \quad (7)$$

Equation (7) allows us, by using experimental data on the integrated intensity I of a cluster luminescence band, to get information on the value of W_{rad}, which reflects the physics of the processes that give rise to the studied radiative transitions occurring in one cluster.

Figure 3 shows integrated intensities of the $(Ar_2)^*$ and $(Ar_4^+)^*$ bands divided by $\ln \bar{N}$ as functions of the average cluster size $\bar{N}$. Each point is the result of averaging over several spectral measurements. Two cluster-size ranges can be seen in Fig. 3 which are characterized by different behaviour of the reduced intensities of both bands.

The large-cluster section ($\bar{N} \geq 1800$ at/cl) displays a nonlinear growth of $I / \ln \bar{N}$ with increasing $\bar{N}$ which can be approximated with good accuracy by $I / \ln \bar{N} \sim \bar{N}^{\alpha}$ with $\alpha = 2/3$ for $(Ar_2)^*$ and $\alpha = 1/3$ for $(Ar_4^+)^*$. It follows from Eq. (7) that $I / \ln \bar{N} \sim \bar{N}^{-1/3} W_{rad}$. This means that the probability of $(Ar_2)^*$ neutral excimers radiating from one cluster is proportional to the total number of atoms in the cluster ($W_{rad} \sim \bar{N}$), while the emission from charged complexes $(Ar_4^+)^*$ depends on the number of atoms contained in some near-surface area of the cluster ($W_{rad} \sim \bar{N}^{2/3}$). Indeed, in case of ionization of an argon atom from

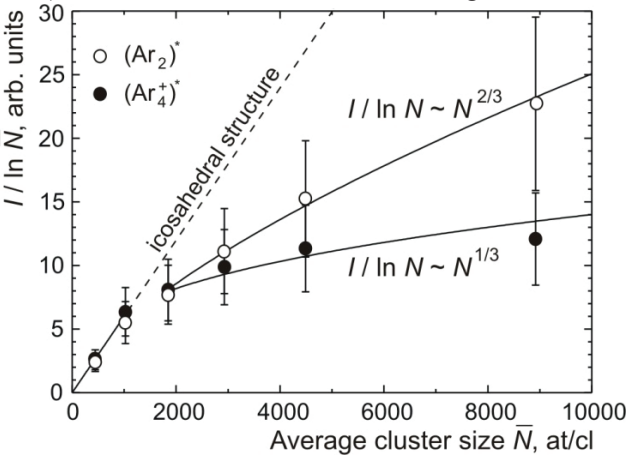

Fig. 3. Average cluster size ($\bar{N}$) dependence of integrated intensity (I) reduced by $\ln \bar{N}$ for $(Ar_2)^*$ and $(Ar_4^+)^*$ bands. Regions of icosahedral structure for $\bar{N} \leq 1000$ at/cl, in which $I / \ln \bar{N} \sim \bar{N}$ for both bands, and fcc structure for $\bar{N} \geq 1800$ at/cl, where $I / \ln \bar{N} \sim \bar{N}^{2/3}$ for the $(Ar_2)^*$ band and $I / \ln \bar{N} \sim \bar{N}^{1/3}$ for the $(Ar_4^+)^*$ band, can be seen.

inner layers of the cluster, the probability of its recombination with the electron before radiation from the $(Ar_4^+)^*$ state is rather high. When an atom from a near-surface layer is ionized, the probability of recombination is lower since the electron is more likely to leave the cluster before it happens.

A different situation is observed for smaller clusters ($\bar{N} \leq 1000$ at/cl). Here, the $I / \ln \bar{N}$ vs. $\bar{N}$ dependences are linear for both bands within the experimental error. It is known from electron diffraction studies that argon clusters of these sizes are quasicrystalline with a 5-fold axis of symmetry (polyicosahedral and multilayer icosahedron structures) [15], while clusters with a few thousands of atoms are characterized by a crystalline fcc structure [16]. If we relate the different behaviour of the reduced integrated intensities of the $(Ar_2)^*$ and $(Ar_4^+)^*$ bands to the cluster structure, we can use our cathodoluminescence data to find the cluster-size range in which a passage from icosahedral (multilayer icosahedron) to crystalline (fcc) structures takes place: we can see from Fig. 2 that it corresponds to $\bar{N}$ = 1000-1800 at/cl. The deviation of the dependences of the reduced intensities for icosahedral clusters towards lower values with respect to their behaviour in the fcc phase can be qualitatively explained by a greater binding energy ε_0 of atoms in an icosahedral cluster [17] (see the factor $\frac{T_*}{\varepsilon_0}$ in Eq. (3)), while the close intensity values for both bands are due to the fact that in small clusters near-surface layers occupy a large fraction of the cluster volume.

Conclusion

We analyze integrated intensities of molecular bands in cathodoluminescence spectra of argon clusters in a wide range of average cluster size $\bar{N}$ from 500 to 8900 at/cl.

Our spectroscopic data demonstrate that the fraction of substance c_{cl} condensed into clusters is proportional to the logarithm of their average size, $c_{cl} \sim \ln \bar{N}$.

It is found that in the case of crystalline fcc clusters of argon with $\bar{N} \geq 1800$ at/cl emission of the vibrationally relaxed neutral excimer molecules $(Ar_2)^*$ comes from the entire cluster ($I / \ln \bar{N} \sim \bar{N}^{2/3}$), while the charged excimer complexes $(Ar_4^+)^*$ radiate from its near-surface layers ($I / \ln \bar{N} \sim \bar{N}^{1/3}$).

The cluster-size range in which a passage from multilayer icosahedron quasicrystalline structure to crystalline fcc structure occurs is determined using the cathodoluminescence technique: it corresponds to the average cluster size values $\bar{N}$ = 1000-1800 at/cl.

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