Photoelectron emission from solid Ne tested by impurity adsorption

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Electron emission was obtained from a solid Ne sample growing from the gas phase on a low temperature substrate. The surface of the sample was irradiated by the light of an open-source microwave discharge running in the gaseous Ne. A second gas flow of CH_4 was, simultaneously, passed onto the substrate avoiding the discharge zone. Free electrons ejected into a vacuum chamber during the sample growth were detected by means of the electron cyclotron resonance (ECR) technique. The electron yield was found to be decrease at increasing CH_4 flow. Fitting curves to the experimental data showed that the surface CH_4 impurities played the major role in emission quenching. A temperature effect was observed in which a 4.2 K sample was much more sensitive to CH_4 doping than a 1.6 K one. Based on the experimental results, a model was proposed of the surface sites where electrons escape the solid.

1. Introduction

In a very recent study [1], an effect has been found that a small gas flow of He provided onto the cold substrate where the gaseous Ne was condensed suppressed the electron photoemission from the solid Ne. It was not clear immediately whether bulk or surface He impurities are responsible for the suppression, though a certain consideration favored the surface effect. Indeed, He atoms trapped in the bulk seem not be able to decrease considerably the yield by quenching Ne excitons through the energy transfer process because of the poor match between atomic He levels and Ne exciton bands. The crucial role of the surface He impurities in quenching photoelectron yield has been verified by fitting experimental curves $A(p)$ [2], where A is the signal amplitude which is proportional to the free electron yield and p is the gas pressure measured at the warm end of the tube supplying the gaseous He to the substrate; the pressure is proportional to the quantity of He flow. To get further in understanding the roles of bulk and surface impurities in the photoemission of free electrons, it would be helpful to test this process using an impurity with lower ionization potential and readily adsorbed by a sample at liquid He temperatures. In the present study, we utilize the molecular CH_4 as such a probe.

The CH_4 impurity may serve not only as a trap for free electrons but, based on its comparatively small ionization potential, may contribute to the free electron production. Indeed, the impurity photoemission threshold is $E_{th}^i = E_g^i + E_a$, where $E_g^i = 12.98$ eV is the methane molecule ionization potential and $E_a = -1.3$ eV is the negative electron affinity of the Ne solid. Then, $E_{th}^i = 11.68$ eV which is smaller than the energy levels of the exciton states of the Ne matrix. In turn, the direct excitation of the impurity state above E_{th}^i by the light of the Ne gas discharge open source used for the sample irradiation in the experiments can contribute to the photoelectric yield. At the first glance, the net effect of the CH_4 doping on the photoelectron yield from solid Ne might be as negative, i.e., decreasing the yield, as positive, i.e. increasing it. However, taking into account the fact that the quantity of electron photoemission from noble gas solids is far above that of molecular solids [3], one would expect a minor contribution of the CH_4 to the yield when compared to the effect of quenching the emission.

2. Experimental details

The electrons escaping into the vacuum from the sample were observed through the electron cyclotron absorp-

tion using a conventional EPR device [1,3]. The setup and experimental procedure have been presented elsewhere [3,4]. Briefly, they were as follows. The bottom of a quartz finger filled with liquid helium served as a low temperature substrate for the gases being condensed. The bottom was located at the center of the microwave cavity of an X-band EPR spectrometer. The cavity was evacuated and cooled externally with liquid nitrogen vapor providing a cavity temperature from 77 to 300 K. An electrodeless high-frequency (15 MHz) discharge operating in pulsed regime was excited in the gaseous Ne which was passed through a glass tube with an outlet of approximately 0.6 mm diameter. The products of the discharge entered the cavity and condensed on the finger bottom, forming Ne solid. The solid was subjected to the action of the irradiation from the outlet, which, thus, operated as an open-discharge source. The methane gas flow was supplied to the substrate by a quartz tube inserted into the cavity. The tube was placed outside the discharge zone. The end of the quartz tube was located close (3 mm) to the substrate. Both gases were cooled with liquid nitrogen vapor prior to deposition. The substrate temperature was lowered down by pumping-out the liquid He bath. The base pressure in the experimental chamber was $2 \cdot 10^{-6}$ torr. Pure gases were used with the following impurity contents: 0.004% Ne and 0.1% CH_4.

3. Results

Figure 1,*a*, solid circles, shows experimental data obtained for the sample temperature of 1.6 K. Also there are shown the fitting curves based on various mechanisms of impurity CH_4 effect on the electron photoemission from solid Ne. The figure suggests decreasing the ECR signal amplitude, *A*, with increasing impurity methane concentration in solid Ne which is proportional to pressure, *p*, measured at the warm end of the tube supplying the gaseous CH_4 to the substrate. Therefore, the major effect of doping Ne with CH_4 is quenching electron emission from the sample. Let us consider first the bulk effect. If *q* is the rate of free electron production in the bulk, *k* is a rate constant which relates to trapping these electrons by CH_4 impurities, and a rate constant k_1 is for the electron loss through emission from the surface, then, in the steady-state condition:

$$q - knN - k_1 n = 0 . \tag{1}$$

Here *n* is the free electron concentration in the bulk, and *N* is the CH_4 concentration.

Hence, the *A(p)* dependence can be written in the form:

$$A(p) = \frac{a_1}{1 + b_1 p} \tag{2}$$

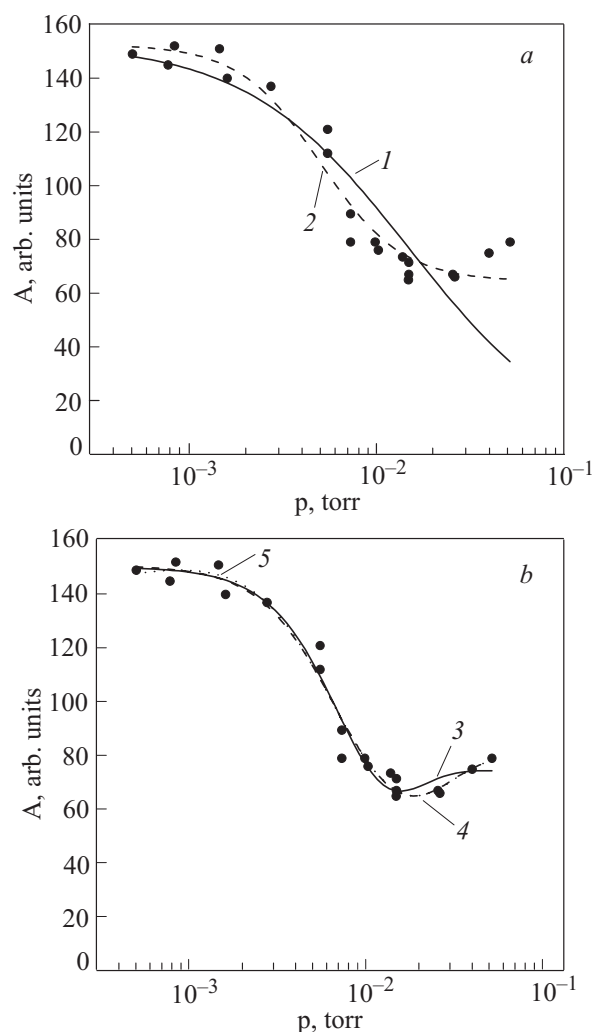with constants a_1 and b_1 to be obtained in the fitting procedure.

Fig. 1. (*a*) The intensity of the ECR signal, *A*, for the 1.6 K sample versus pressure, *p*, measured at the warm end of the tube supplying the gaseous CH_4 to the substrate. Filled circles — experimental data; fitting curves: *1* — calculated in assumption that bulk CH_4 impurities play major role in photoemission quenching, *2* — suggests a major role of the surface CH_4 impurities. (*b*) The theoretical curves for *A(p)* dependence based on the assumption that the surface CH_4 impurities play a key role in emission quenching; the experimental points are the same as presented in Fig. 1,*a*; these experimental data are fitted with curves: *3* and *4* account for CH_4 microcrystal formation with and without a component independent of the pressure *p*, respectively, *5* — accounts for both the CH_4 microcrystal formation and the direct ionization of the impurity CH_4 molecules.

The dependence is plotted in the Fig. 1,*a*, providing rather poor match to the experimental results, especially at moderate and large CH_4 flows.

Another model deals with surface CH_4 impurities, suggesting that the electron emission into the vacuum proceeds from the Ne surface free of adsorbed CH_4 mole-

cules. Let S_{free} and S_{occup} be the surface areas which are free of adsorbed CH_4 atoms or occupied by these atoms, respectively. It is reasonable to assume that $S_{\text{free}}/S_{\text{occup}}$ is proportional to p_{Ne}/p_{CH_4}, where p_{Ne} is the gaseous Ne pressure in the cavity and p_{CH_4} is the methane pressure:

$$S_{\text{free}}/S_{\text{occup}} = \gamma p_{\text{Ne}}/p_{CH_4} . \qquad (3)$$

Here γ is the proportionality coefficient. Taking into account that $S_{\text{free}} + S_{\text{occup}} = \text{const}$, one concludes:

$$S_{\text{free}} \sim \left(1 + \frac{p_{CH_4}}{\gamma p_{\text{Ne}}}\right)^{-1} . \qquad (4)$$

Based on the suggestion that A and p_{CH_4} are proportional to S_{free} and p, respectively, we again come to the above $A(p)$ dependence, Eq. (2). Therefore neither bulk CH_4 impurities nor those on the flat surface are responsible for quenching electron photoemission.

Next we test the model which applies well to photoemission from solid Ne quenched by impurity He [2]. We used expression for $A(p)$ modified as follows [2]:

$$A(p) = \frac{b_2}{1 + c_2 p^{d_2}} + a_2 . \qquad (5)$$

Equation (5) was obtained under suggestion that the surface He atoms play the major role in quenching photoemission. The component a_2 accounted for the fact that, due to new layers of solid Ne appearing again and again during condensation, the part of the sample surface had high enough temperature not to adsorb He atoms. Therefore, no He «screening» occurred at these areas and the electrons were allowed to live the sample. Fitting procedure gave the best value for d_2 close to 2. An analysis of the value of d_2 led to the conclusion that the electrons escape the sample from special regions on the surface nearby the lines where two Ne planes cross and these regions are, possibly, atomic step sites (step edges) at the Ne surface which are responsible for the sample growth. Now, we apply Eq. (5) with $d_2 = 2$ to fit the experimental data for photoemission from solid Ne quenched by CH_4 impurities. Curve *2* (Fig. 1,*a*) presents a result of the fitting procedure which suggests that we arrive at a reasonable agreement between theory and experiment for small and moderate CH_4 flows. The physical meaning, however, of the component a_2 is not as clear as in the case of the He impurity. Another difference between the present experimental results and those of Ref. 2 is a trend to slightly higher A values at large flows observed for the CH_4 impurity and not observed for the He impurity. One may suppose that at large CH_4 flows solid methane microcrystals start to be formed, which (being subjected to UV radiation) contribute to photoelectron emission. It is reasonable to assume that the CH_4 crystal concentration is proportional to $p^{d_3}/(1 + k_2 p^{d_3})$ with $d_3 \approx 2$. We have

no suggestion at the moment about the exact value of d_3. However, the fitting shows that d_3 may vary across a large range and, for example, quadratic pressure dependence, p^2, leads to result which differs insignificantly from that of the cubic one, p^3. Let us assume $d_3 = 3$. Curves *3* and *4* (Fig. 1,*b*) are plotted using Eqs. (6) and (7), respectively, which account for CH_4 microcrystal formation:

$$A(p) = \frac{a_3}{1 + b_3 p^2} + \frac{c_3 p^3}{1 + e_3 p^3} , \qquad (6)$$

$$A(p) = a_4 + \frac{b_4}{1 + c_4 p^2} + \frac{e_4 p^3}{1 + f_4 p^3} . \qquad (7)$$

It is readily seen from the Fig. 1 that the component a_4 (independent of pressure p) has almost no effect at low and moderate CH_4 flows. On the other hand, curve *4* fits better to the experimental data which means that some third component should be presented in the $A(p)$ expression and this component is linked to the methane flow. We suppose that this component accounts for the direct ionization of the impurity CH_4 molecules and is proportional to $p/(1 + k_3 p)$. In this way we come to the following expression for $A(p)$:

$$A(p) = \frac{a_4}{1 + b_4 p^2} + \frac{c_4 p^3}{1 + e_4 p^3} + \frac{f_4 p}{1 + g_4 p} . \qquad (8)$$

Curve *5* (Fig. 1,*b*) plotted using Eq. (8) fits well to the experimental data. At moderate and large CH_4 flows it overlaps curve *4* thus making these two curves undistinguishable.

For 4.2 K samples, Fig. 2, the overall trend resembles that of 1.6 K. The major difference is in that the observed signal amplitude decreases with increasing CH_4 flow much more rapidly as compared with the process at 1.6 K.
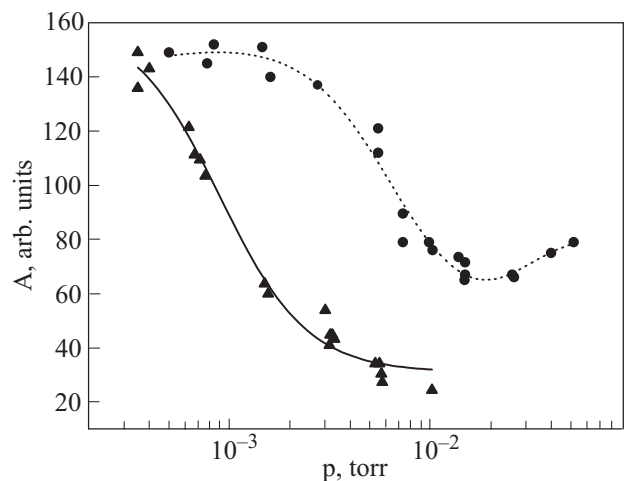

Fig. 2. The intensity of the ECR signal, A, versus pressure, p, measured at the warm end of the tube supplying the gaseous CH_4 to the substrate: triangles — the 4.2 K sample, circles — the 1.6 K samples.

The CH_4 microcrystal formation is not seen in 4.2 K experiments. This obviously is due to relatively small methane flows in the experiments. Henceforth, we modify the fitting Eq. (8) by removing the second component:

$$A(p) = \frac{a_5}{1 + b_5 p^2} + \frac{c_5 p}{1 + e_5 p}. \tag{9}$$

An agreement between the theoretical model and experiment, Fig. 2, may be considered as rather good. For comparison, the 1.6 K data are also presented in the figure.

4. Conclusion

The present study revealed that the net effect of doping by an impurity with relatively small ionization potential on the photoelectron yield from the solid Ne is to decrease the free electron emission. Though the bulk CH_4 impurities are believed to take some part in quenching emission, their influence was not elucidated. The major role is played by the surface CH_4 molecules. Interestingly, the same inference was made for the solid Ne–He impurity system. The similarity in emission behavior under doping with such a different species like He and CH_4 deserves special attention. It is known that electrons are not self-trapped in matrices like Ar [5] and Ne due to negative electron affinities of these matrices. In nominally pure matrices the electrons can be trapped only by such lattice defects as vacancies, vacancy clusters or pores [5]. It is thought that the defects are relatively shallow traps, while much deeper traps could be a guest atom or molecule with positive electron affinity [5]. The atomic He, however, is a particle with very small positive affinity, 0.0054 Ry [6] which is equal 0.073 eV, and CH_4 molecule has negative electron affinity, $E_a = -5$ eV [7,8]. The mechanism for the decrease in electron emission by impurity particles in our experiments is not clear at present. One of the propositions for this mechanism is that, despite the affinities of different signs, both He and CH_4 impurities turns out to be effective traps in solid Ne, which scavenge electrons, thus not allowing them to escape into the vacuum. The observed effect is related to the processes of electron trapping in insulator materials [8,9]. The authors established a relationship between the electron trap and the molecular properties of the material. They studied both physical (e.g., conformational disorder) and chemical defects (e.g., broken bonds and impurities) and showed that while typical physical trap energies were of the order of 0.15 eV and all are less than 0.3 eV (for polymeric insulators), the chemical defect trap energies reached about 1 eV even for impurities with negative electron affinity for free molecules [9]. The trap energy, E_{trap}, was defined as the energy difference between the electron affinity of the system with and without the defect, thus

$$E_{trap} = E_{a\,defect} - E_{a\,reference}. \tag{10}$$

Another proposition for the quenching mechanism of electron emission by impurities is that the electron affinity of the impurity does not account for the effect, i.e., a surface impurity of any kind may prevent bulk electrons from appearing at the surface. To check this assumption, additional experiments using impurities with positive affinity, like O_2, $E_a = 0.44$ eV [10], NO_2, $E_a = 2.43$ eV [10], as well as those with negative affinity, H_2 and CO, $E_a = -1.8$ eV [11], are in progress. When compared to each other, the results will give us an answer to the problem whether the electron affinity of an impurity links to the quenching electron photoemission from solid Ne.

The present experimental results for the CH_4–Ne system and those reported earlier for He–Ne one [1] differs significantly in the temperature behavior of the photoemission. Indeed, the Ne–He pair showed a faster drop in the photoelectron yield for the 1.6 K samples as compared to the 4.2 K ones, while an inverse situation was observed for the Ne–CH_4 pair. At 4.2 K, He atoms have too small adsorption time on step sites where, possibly, the electron emission occurs. The adsorption time grows exponentially with lowering temperature. That is why He impurity has much more prominent effect on the photoelectron yield for the 1.6 K sample as compared the 4.2 K one. The situation for CH_4 is quite different, with long adsorption time at both temperatures. The observed temperature effect can, therefore, be explained by changing sample quality at different deposition temperatures. In a recent paper [12], the temperature stimulated luminescence and temperature stimulated exoelectron emission from solid Xe pre-irradiated by low-energy electrons were found to be sensitive to the sample deposition temperature. The authors pointed out that the effect is explained with growing number of lattice defects on lowering deposition temperature. These defects serve as shallow traps for electrons. Therefore, it is stressed [12] that the more defects in the crystal, the lower concentration of electrons escaping from traps at low temperatures and vice versa. In our experiment with impurity CH_4, low deposition temperature favors electron emission which is evident from the fact that quenching emission by the impurities at 1.6 K is less effective than at 4.2 K. We suggest that low deposition temperature leads to larger number of steps on the Ne surface and that more CH_4 flow is necessary to block emission occurring, as we suppose, from these steps. The suggestion may be verified in experiments with other impurities which are also readily adsorbed at liquid He temperatures. Similar temperature behavior for all these kinds of impurities would verify the suggestion.

Doping of Ne may lead not only to a decrease of electron emission but also to its increase. It follows from examining of Eqs. (8) and (9) that at moderate impurity

flows $A(p)$ may increase reaching a maximum. Whether the gains in emission can be significant remains to be seen in experiments which are planned now.

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