
Measurements of Cu Atoms Diffusion Coefficients in He and Ne — Optimalisation of a Novel Method

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A novel method based on two-pulse excitation of a hollow cathode discharge to determine metal atoms diffusion coefficients in noble gases was tested in Cu–He and Cu–Ne systems. The excitation conditions such as time duration of the discharge current pulses and configurations of the hollow cathode discharge were checked. Measurements carried out over the wide range gas pressures allowed obtaining the Cu atoms time-decay curves from which the diffusion coefficients were calculated. The values for Cu atom diffusion coefficients of 570 and 310 cm² s⁻¹ mbar in He and Ne, respectively were in a good agreement with earlier reported data achieved by using the absorption spectroscopy method. The diffusion coefficient of Cu in ³He, the lighter isotope of helium, was also found to be 670 cm² s⁻¹ mbar that agreed well with the kinetic theory of gases. To authors believe this value was not reported previously.

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1. Introduction

Diffusion of metal atoms in different gases is essential not only in noble gases — metal vapour lasers (MVL) operating on either ionic or atomic transitions but also in all techniques involving plasma sputtering, e.g. a thin-layer deposition. However, determination of the diffusion coefficients, particularly for atoms of high-melting-point metals in noble gases, is rather complicated and only limited information is available in the literature. Experimental diffusion coefficients have been reported for copper atoms in He [1, 2], Ne [2, 3], Ar [2, 4] and

Kr [5]. Semiempirical calculations of Cu atoms diffusion coefficients in rare gases can also be found in [6]. In all the cases but one [4], a sputtering of copper cathode walls in a pulsed hollow cathode discharge (HCD) was used to produce copper atoms. After termination of the current pulse their time-dependent density was measured by the absorption spectroscopy method. From the slopes of metal atom decay curves and for given geometry of the discharge chamber, gas pressures and temperature the metal atom diffusion coefficients were calculated. The absorption measurements require additional source of radiation that emits the wavelengths corresponding with the resonant lines of the metal atoms in the absorption cell. However, to ensure the correct relations between measured absorption of the resonant radiation and density of ground state metal atoms, the spectral distribution of the emitter line should be identical or at least very similar to the distribution of the resonant transition in the investigated medium. The calculations of the metal atom densities require a special computer program in which the oscillator strength of the resonant transition, its hyperfine structure and isotope shift have to be taken into account. For example, in [1] 12 hyperfine transitions forming two resolvable components of the 324.8 nm Cu I resonant line had to be used in the calculations.

A novel method of determining metal atom diffusion coefficients in noble gases was proposed in [7]. The method was based on two-pulse excitation of a HCD metal ion laser in which thermal energy charge-transfer (C-T) collisions between noble gas ions and metal atoms sputtered from the cathode walls led to the selective population of the upper laser levels. The method was experimentally verified in [8] for a He-Cu ion laser operating on the 780.8 nm Cu II transition giving the correct value of Cu diffusion coefficient in He. In the next work [9], this method was further extended by including measurements of spontaneous emission from the levels pumped by the C-T reaction. The intensity of laser action as well as spontaneous emission from those levels is proportional to density of metal atoms in the discharge volume. Hence, measuring of the laser action or spontaneous emission intensities caused by the second pulse versus time delay between the pulses allows to establish the decay curves of the ground state metal atoms in the afterglow. From the negative slope of the curves the diffusion coefficients are calculated in similar way as in the absorption method. This method is rather simple and does not have inconveniences of the latter.

In this paper we present the optimisation of the developed method for Cu-He and Cu-Ne mixtures. Moreover, the diffusion coefficient of Cu atoms in the lighter helium isotope ^3He was also measured. Its value was about 15% higher than that for ^4He , which agreed well with the kinetic theory of gases.

Section 2 of this paper describes the idea of the method. The experimental arrangement is shown in Sec. 3. The results of the measurements are presented and discussed in Sec. 4. Section 5 summarizes the results of this work.

2. Description of the method

In sputtered HCD lasers metal atoms are produced by ion bombardment of the cathode walls. They thermalise after short distance from the cathode surface, then diffuse toward the centre of the discharge. For many metal ion laser systems they are ionised and excited to the upper laser levels by the asymmetrical thermal-energy C-T collisions with noble gas ions



where B, B⁺ represent noble gas atoms and ions, Me and Me^{+*} are ground state metal atoms and ions excited to the upper laser level, and ΔE is the energy defect.

The rate constant R_{C-T} of the selective population of the upper laser levels is proportional to the densities of colliding particles, their mutual velocity v , and the C-T cross-section σ_{C-T} :

$$R_{C-T} = v\sigma_{C-T}N_{Me}N_{B^+}. \quad (2)$$

The intensity of laser and/or spontaneous emission from the metal ion levels excited by the C-T reactions is directly proportional to the R_{C-T} constant, hence, to the density of metal atoms in the discharge volume providing the buffer gas ion density is kept constant.

When pairs of current pulses excite a HCD laser, the first pulse serves as a source of metal atoms. The time duration of each pulse is too short for metal atoms to reach the centre of the hollow cathode and support laser action for the buffer gas ions, which are responsible for their excitation to the upper laser levels and disappear quicker. The second pulse applied some time later encounters sufficient amount of metal atoms and the laser generation occurs. The intensity of the laser oscillations is proportional to the metal atom density in the region of the laser beam and varies with the time interval between two pulses. From the declining slope of the laser power versus time delay between the pulses, the characteristic diffusion times can be found, and for known dimensions of the hollow cathode and noble gas pressure, the diffusion coefficient of the investigated metal can be calculated. Similar principle applies for intensity of the spontaneous emission from the levels populated by the C-T reactions.

If the discharge region has cylindrical geometry and its length is much larger than diameter of the cathode, the metal atom density has only a radial spatial dependence and is determined by the diffusion equation

$$\frac{\partial n(r, t)}{\partial t} = D \left[\frac{\partial^2 n(r, t)}{\partial r^2} + \frac{1}{r} \frac{\partial n(r, t)}{\partial r} \right]. \quad (3)$$

The solution of the above equation, with the same assumptions as made in [1], during the active discharge gives the initial density distribution of metal atoms sputtered from the cathode walls by the first current pulse. The thermalization of the metal atoms leaving the cathode surface with energies even on the order

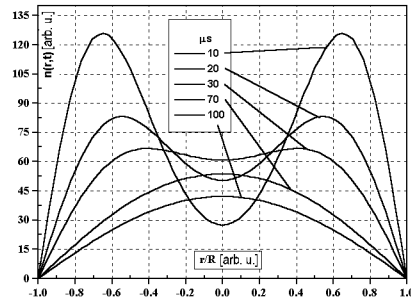


Fig. 1. Spatial density distribution of copper atoms in He calculated after termination of the first discharge current pulse.

of 1 eV [10], change a little this distribution but can be neglected providing gas pressure is high enough as was estimated in [1]. Again, the solution of the diffusion equation in the afterglow phase yields a very important information about the changes of the metal atom density distribution within the time interval between the pulses. Calculated radial density profiles of Cu atoms in He at various times after termination of the first pulse are shown in Fig. 1.

It can be seen that after several tens of microseconds the copper atoms in the tube volume diminish according to the fundamental diffusion mode. By integrating the density profiles the changes in relative number of Cu atoms in the tube cross-section can be found. In Fig. 2 they are presented in semilogarithmic scale for three different He pressures. Again, after 50–70 μs the number of Cu atoms decreases exponentially, i.e. in the fundamental diffusion mode, and decay time constants τ can be determined from declining slope of the curves.

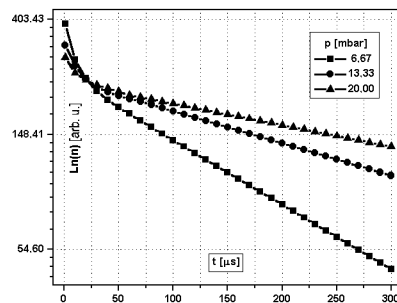


Fig. 2. Calculated relative changes of the number of Cu atoms in the afterglow.

For cylindrical geometry the time constants representing the average lifetime of Cu atoms in the tube volume are connected with their diffusion coefficient by the following expression:

$$D_0 \left(\frac{p_0}{p} \right) \left(\frac{T}{T_0} \right)^{\frac{3}{2}} \tau = A^2, \quad (4)$$

where D_0 is the diffusion coefficient of Cu atoms in He at standard conditions ($T_0 = 273$ K, $p_0 = 1$ mbar), T and p are He temperature and pressure. A is the characteristic diffusion length, and for a cylindrical hollow cathode with the length L and inner diameter R , can be calculated from the expression

$$A^2 = \frac{1}{\left(\frac{\pi}{L} \right)^2 + \left(\frac{2.405}{R} \right)^2}. \quad (5)$$

This is only true if it is assumed that all Cu atoms striking the cathode surface remain there, i.e. that the reflection of metal atoms from the cathode walls is 0. When the reflection coefficient is higher, τ represents only real decay times of metal atoms in a gas chamber combining both processes — diffusion to the walls and reflection from them. In all previous works the diffusion coefficients of Cu atoms in noble gases were determined under the assumption that their reflection coefficient at the walls is equal to zero. Only in [11] Rusinov et al. proposed a method for simultaneous evaluation of metal atoms diffusion coefficient and their reflection from the walls.

However, the aim of this work was to compare the results obtained using the new method with those reported in [1–6] under the same boundary conditions.

The fundamental difference between the absorption spectroscopy method and this one lies in the way in which the changes of the density or number of metal atoms created by the first current pulse are monitored. In the absorption spectroscopy the relative changes of metal atom density in the investigated medium are determined by measuring the absorption of resonant radiation from the external source. In the method described here the intensity of laser action or spontaneous emission from the levels populated by the reaction (1) is proportional to the pumping rate (2), and hence, to the density or number of metal atoms (old and new) in the discharge volume. However, there is a significant difference between the monitoring the laser intensity and the spontaneous emission. In the first case the laser intensity is proportional to number of excited metal ions within the region of the laser beam, i.e. in the centre of the hollow cathode. The discharge pulse is too short for the noble gas and metal ions to reach the cathode walls and sputter more metal atoms which in turn could diffuse into the generation region. In the second case the situation is different because the spontaneous emission signal is radiated from the whole cross-section of the discharge. Hence, the spontaneous emission is observed even for short time discharge pulses because the C–T collisions occur also close to the cathode walls. To establish the decay curves of the metal atoms the emission caused by the first current pulse is used as the reference intensity, which requires the second current pulse to be of the same amplitude and width as the first one. The number of photons produced by the C–T reaction during the second discharge pulse consists of the new ones and of those coming from the residual metal atoms left in the tube by the first pulse. Moreover, the

“old” metal atoms transferred into ions can reach the cathode surface and sputter additional metal atoms, which may undergo the C–T collisions close to the cathode walls and also contribute to the total signal. However, it must be stressed that this additional multiplication of the photon production due to a rise of the cathode-sputtering rate by the “old” ions is still proportional to the number of metal atoms remaining in the gas volume after termination of the first pulse. The spontaneous emission intensities are usually detected using a monochromator and a photomultiplier. An integral over the shape of the photomultiplier signal is a measure of a number of photons reaching its photocathode. Therefore, each pair of the spectral emission pulses has to be integrated and the difference between integrals of the second and first light emission pulses is proportional to the number of additional photons created from metal atoms remaining in the tube after the first discharge pulse.

3. Experimental setup

The measurements of copper atoms decay curves were carried out using a segmented hollow cathode discharge (SHCD) tube. The cathode and anode segments of the tube were made of an oxide free high conductivity (OFHC) copper rod. The four electrodes isolated from each other by ceramic spacers were stacked together creating 5 cm long discharge volume with 8 mm internal diameter, though the total volume of the test tube exceeded 10 cm³. Auxiliary cylindrical anodes were put on both ends of the segment module. The more detailed description of the tube design can be found in [12].

By switching electrical connections of the segments and the additional anodes three different discharge configurations could be obtained: the cylindrical, perpendicular and segmented HCD without changing the gas chamber geometry — see Fig. 3.

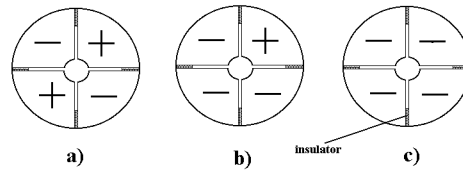


Fig. 3. Configurations of the hollow cathode discharges: (a) segmented HC, (b) HC with perpendicular geometry, (c) cylindrical HC.

The scheme of the experimental arrangement is shown in Fig. 4. A pulse power generator built with fast insulated gate bipolar transistors (IGBT) excited the discharge tube with pairs of high voltage rectangular pulses whose amplitudes could be independently regulated as well as their length and interval between them. The repetition rate of the pulses was low (5 Hz) in order to avoid gas heating.

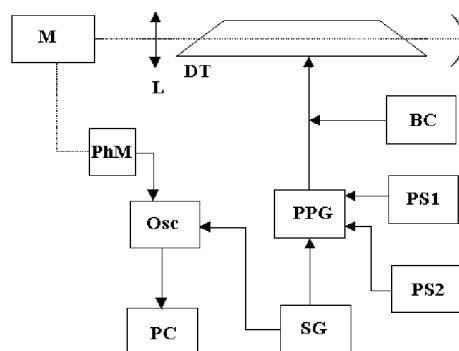


Fig. 4. The block scheme of the experimental arrangement.

A very low (much under 1 mA) DC discharge current was sustained to improve discharge stability. According to a rough estimation, the power dissipated in the discharge tube was less than 0.2 W for the DC excitation and up to 0.3 W for double-pulse operation at the longest pulse duration and the highest voltage of the segmented HC discharge. Taking into account a relatively large volume of the tube and a bulky electrode construction the assumption that the gas temperature was close to 300 K was justified.

Light from the discharge tube was focused on the entrance slot of an UV Czerny–Turner monochromator with dispersion 2 nm/mm in the spectral range 200–800 nm. Intensities of the Cu II transitions populated by the C–T collisions with He and Ne ions were measured using the R 325 Hamamatsu photomultiplier. The signals from the photomultiplier were displayed on the screen of an Agilent Techn. 54622A oscilloscope together with pairs of the discharge current pulses. The oscilloscope input RC time constant was chosen large to smooth the shapes of the spontaneous emission pulses. The measurements were performed for the time delay between the pulses varying from 60 to 320 μs with 20 μs step. For each step discharge current and light pulses were averaged over 2^{14} runs and fed to a PC computer.

4. Results and discussion

The testing and optimisation of the method was carried out for Cu–He and Cu–Ne mixtures for diffusion coefficients of copper atoms in both gases are well known. The intensities of the spontaneous emission was measured for Cu II, 780.8 and 270.3 nm transitions populated by the C–T collisions with He and Ne ions, respectively. Typical trains of the 780.8 nm, Cu II line intensities and discharge current pulses are presented in Fig. 5. For clarity reason only every second step is displayed. It is worth mentioning that no other transmissions coming from Cu I and Cu II levels directly excited by electrons show the same behaviour. The longer time

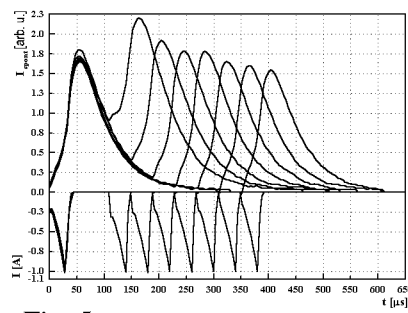


Fig. 5

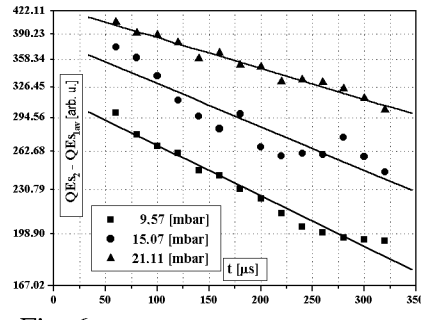


Fig. 6

Fig. 5. Trains of the spontaneous emission and discharge current pulses.

Fig. 6. The Cu atom decay curves vs. time delay between discharge pulses.

duration of the light pulses is caused by the large time constant RC. In Fig. 6 the Cu atom decay curves obtained from differences between integrals of the second and first light emission pulses are presented in the semilogarithmic scale versus time interval between the current pulses for one of the measured series.

The most important parameter, which required optimisation in the described method, was the time duration of the current pulses. It could be observed that when a rectangular high voltage pulses were applied to the electrodes of the discharge tube the current started flowing after a few to several microseconds delay which could not be controlled. Hence, the length of the current pulses could not be chosen too short, i.e. $20 \mu\text{s}$ as it was in [10]. On the other hand, too long pulses diminish the resolution of the method. Therefore, the discharge was excited by pairs of current pulses with 1 A amplitude each, and the duration time of 30, 40, and $50 \mu\text{s}$, respectively. The amplitude of the discharge pulses was not critical. It was chosen low enough to avoid gas heating and, simultaneously, to obtain a fair signal from the photomultiplier. The emission light caused by the first current pulse was used as the reference intensity in calculating the decay curves; hence, it was necessary to hold the same amplitude of the second pulse while scanning the afterglow. Due to residual charges left in the gas volume by the first pulse, particularly in the time range up to about several tens of μs , the voltage of the second pulse had to be slightly adjusted to keep the same current amplitude for both pulses. The required voltage changes were much less than 1% of the total discharge voltage, mainly at earlier stages of the afterglow, and therefore, should not affect the sputtering rate of the metal atoms for the measurements started $60 \mu\text{s}$ after termination of the first pulse. The diffusion coefficients of Cu atoms in He and Ne determined for several gas pressures and the three different lengths of the discharge pulses are shown in Figs. 7 and 8. As it can be seen, in the investigated range of the pulse duration, the obtained results are in a good agreement with previously reported data.

The influence of the HCD configurations on possibility of determining dif-

fusion coefficients was also tested. Figure 9 shows that geometry of the discharge

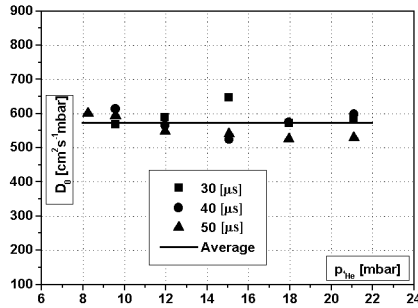


Fig. 7

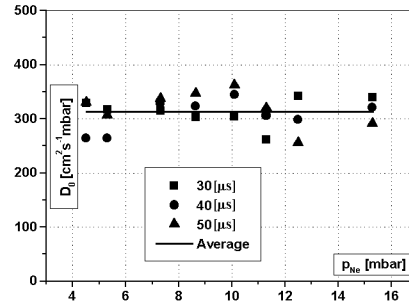


Fig. 8

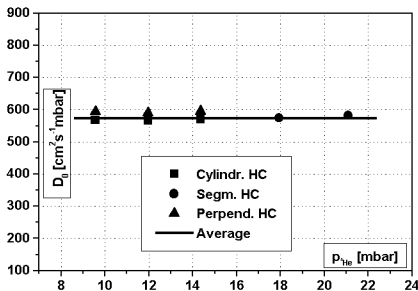


Fig. 9

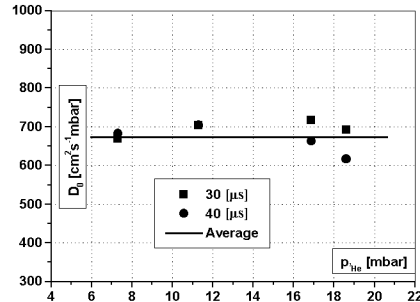


Fig. 10

Fig. 7. Diffusion coefficients D_0 of Cu atoms in ^4He for three time-durations of the discharge pulses.

Fig. 8. Diffusion coefficients D_0 of Cu atoms in Ne for three time-durations of the discharge pulses.

Fig. 9. Diffusion coefficients D_0 of Cu atoms in ^4He for different configurations of the HC discharge.

Fig. 10. Diffusion coefficient D_0 of Cu atoms in ^3He .

did not affect the results of measurements because the discharge volume was the same for all configurations.

Finally, the diffusion coefficient of copper atoms in the lighter isotope of helium — ^3He was determined. Two series of measurements were carried out for four different pressures of almost pure (97%) ^3He — 7.3, 11.3, 16.9, and 18.6 mbar, respectively. The diffusion coefficients D_0 of Cu atoms in ^3He were calculated for each of the investigated pressures and measurement series — see Fig. 10. The averaged value of D_0 was equal to $670 \pm 65 \text{ cm}^2 \text{ s}^{-1} \text{ mbar}$.

In the case of self-diffusion and the mutual diffusion of two dissimilar gases when the relative concentration of one of the gases is vanishingly small, the kinetic theory of gases predicts the diffusion coefficient to be proportional to the mutual velocity of both kinds of particles. In the case of Cu atoms diffusing in He the

replacement of the normal ^4He by ^3He decreases the reduced mass of the Cu–He system to $3/4$, so then the mutual velocity increases by about 15%. Therefore, the diffusion coefficient of Cu in ^3He isotope should be about $680 \text{ cm}^2 \text{ s}^{-1} \text{ mbar}$. The obtained result is in good agreement with this prediction.

The values of Cu diffusion coefficients D_0 in ^4He , ^3He and Ne are listed in Table together with the results obtained by other authors. They were calculated assuming the gas temperature equal to 300 K.

TABLE
Diffusion coefficients D_0 of Cu in He and Ne (given in $\text{cm}^2 \text{ s}^{-1} \text{ mbar}$).

	Cu– ^4He	Cu–Ne	Cu– ^3He
This work	570 ± 75	310 ± 60	670 ± 65
Other results	572 [4], 560 [5], 576 [7], 572 [9]	293 [6], 253 [5], 205 [7]	–

Summarising, the accuracy of this method in determining the diffusion coefficients varies between 10 and 20% depending mainly on stability of the discharge and reproducibility of the discharge pulses, e.g. the stability of the HCD in Ne is much worse than in He. The reproducibility of the pulses might be improved by increasing the DC bias current, though it would increase the gas temperature and, therefore, complicate the calculations. It is worth mentioning that the accuracy of the absorption spectroscopy method is of the same order.

5. Conclusions

The method of determining diffusion coefficients of metals in noble gases by two-pulse excitation of a HC discharge has been proven to be useful. This method can be applied to every sputtered metal atom–noble gas system in which the charge–transfer collisions of the ground state noble gas ions with metal atoms occur. Particularly, it can be applied to the sputtered metal ion HCD lasers where the knowledge of diffusion coefficients of the particles (metal atoms, ions and noble gas ions) is important. To the authors best knowledge the diffusion coefficient of Cu in ^3He has not yet been reported.

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