NEUTRAL ATOMIC CENTERS IN AMORPHOUS SYSTEMS

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The decay kinetics of neutral paramagnetic atomic centers, measured by EPR, is shown to be an useful tool and perhaps the first direct experimental method to study the size distribution of the bridging oxygen ring structures throughout the continuous random network of an amorphous matrix. The trapping sites for the neutral atoms can be classified into two major groups. The first one comprises an open set of polygons or ring structures of matrix atoms having sufficient polarizability to hold trapped neutral atoms by means of Van der Waals forces, at temperatures below ≈ 220 K. The second group is characterized by a set of matrix atoms enclosing the atomic centers into cages of relatively higher stability, often reaching temperatures far above room temperature (≤ 450 K). Representative examples are presented and discussed, showing how the experimental kinetic approach contributes to a better understanding of the mechanisms involved in structural changes induced by the thermal history of an amorphous solid.

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1. Introduction

Several early examples of neutral atomic centers are well known, such as those found in the extensive literature on electron paramagnetic resonance (EPR) of neutral atomic centers stabilized in crystalline and amorphous host matrices. However, the nature of the trapping dynamics and the associated structural properties of the trapping sites in noncrystalline stabilizing sites are still controversial. Unlike as the crystalline hosts where the superhyperfine structure of paramagnetic centers was observed giving very detailed structural information regarding the positions of the atoms in the lattice, such favourable conditions were not found in amorphous host materials, remaining only the ordinary hf's carrying relatively much poorer local information. Growth and decay kinetics of the neutral paramagnetic centers, induced by ionizing radiation and then submitted to specific heat treatments, provide additional useful information to obtain perhaps unique experimental data to probe the main random network and molecular models of ring structures with oxygen atoms occupying the corners [1].

Hydrogen, the simplest of the atoms of the periodic table of elements [2-20], enters the glasses and other amorphous materials forming covalent bonds with the network forming elements, appearing combined with oxygen as hydroxyls and hydrogen bonds [21,22], or passivating dangling bonds as in the semiconducting thin films [23,24]. The neutral H⁺ centers are induced by means of radiolytic irradiation, together with protons and H⁺.

Metal ions can occupy can occupy exclusively modifying position like Ag⁺, or both substitutional and modifying positions, like Al³⁺, Fe³⁺, or Cr³⁺. Under exposure to ionizing irradiation, they can be oxidized or reduced, trapping holes or electrons, respectively. The neutral Ag⁺ center is readily obtained from the reaction of the Ag⁺ with a photoelectron [25-32].

It is the purpose of this article to show, by means of some examples selected from previous work on atomic hydrogen observed in X-irradiated hosts of insulating BABAL glasses [33-35], how
the H\textsuperscript{0} thermal kinetics can be used to obtain perhaps unique informations about the nature and distribution of oxygen ring structures in the matrix network, as well as to describe the nature of the sites for the neutral hydrogen stable at higher temperatures, found in an amorphous semiconductor a-Si:[N,O,H] thin film [36-37] and the crystalline minerals beryl [38] and pink tourmaline [39]. The latter H\textsuperscript{0} centers are assumed to be enclosed in cages of neighbouring oxygen atoms.

2. The mechanisms of stabilization of neutral atomic centers in amorphous and crystalline host matrices

Our previous studies of defects in crystals and amorphous materials suggested that the kinetics of the defect concentrations can be described through coupled differential equations [40]. The solution of the system of the equations, carried out by numerical analyses using the Runge-Kutta (RK) method [41], were in good agreement for large values of time for the isothermal decay data. In order to overcome some unstabilities for short times, an approximate solution applying the Poincaré-Dulac theorem [42] to the Newton-Raphson method to deal with complex systems involving a large number of coupled differential equations. The experimental data of thermal decay of H\textsuperscript{0} found at different examples of materials can be classified in two groups, according to their limiting stabilization temperature: (a) below and (b) above $T \approx 230$ K.

It is shown below that the atomic hydrogen, the simplest of the elements of the periodic table, can be used as a probe to check the models of local structures, based on specific interactions, such as the Van der Waals attractive forces and Pauli repulsion interactions [5] to account for the possible stabilization mechanisms in oxide glasses. For the remaining group of H\textsuperscript{0} and Ag\textsuperscript{0} centers, stable above room temperature, it is assumed that the neutral atoms are imprisoned in cages to be investigated in each particular case. Some representative examples of H\textsuperscript{0} and Ag\textsuperscript{0} trapping are presented below in order to compare some experimental thermal decay kinetic data with the nature of the mechanisms for the centers stabilization.

2.1. H\textsuperscript{0} trapped in BABAL glasses [33-35]

As example of group (a), Fig. 1 shows the EPR measurements of isochronal thermal decay of H\textsuperscript{0} centers trapped in BABAL glasses X-irradiated at 77 K, of successive temperature pulses of 10 minutes at intervals of 20 K, for different times of exposure to a (20 kV; 40mA) tungsten target X-ray beam [33].

Two main features were observed in the behavior of the isochronal thermal decay of H\textsuperscript{0} at the given BABAL glass sample:
1) all the decay curves vanished at $T = 230$ K;
2) the decay curves of the sample for different times of exposure to the irradiation showed the occurrence of different conditions of stabilization for a given range of the temperature pulses.

The relatively low stability of the H\textsuperscript{0} centers, trapped in barium aluminoborate glasses, leads to the suggestion that the attractive Van der Waals interaction is the predominant trapping mechanism for $T \leq 230$ K. The neutral atomic hydrogen atoms are trapped and/or released most readily from the shallow traps, reaching successively deeper and more stable trapping sites, unless a recombination occurs. The shallower traps have the larger capture cross-sections.

The quantitative depth values for a number of H\textsuperscript{0} sites in a BABAL glass were determined by performing a set of measurements of isothermal decay at temperatures chosen in the range of maximum slope of the isochronal decay curve [33] (see Fig. 2).
Fig. 1. Isochronal thermal decay of $\text{H}^0$ center in BABAL glass X-irradiated at 77 K, of successive temperature pulses of 10 min [33].

Fig. 2. Isothermal decay of $\text{H}^0$ center at 198 K in a BABAL glass, showing its graphical separation into three exponential functions [33].

The isothermal decay was obtained for selected temperatures at different steps selected from the isochronal decay curve. The experimental curve was decomposed graphically in three exponential functions:

$$I_0 = \sum_{j=1}^{3} a_j \exp[-b_j t]$$

(1)

where $I_0$ and $a_j$ are amplitudes proportional to the $\text{H}^0$ concentration at the time $t$,

$$b_j = b_{0j} \exp[-E_j / kT]$$

(2)

where $b_{0j}$ is the pre-exponential of frequency factor of the $\text{H}^0$ in the $j$-th site, and $k$ the Boltzmann constant. The values $a_j$ and $b_j$ were obtained from experimental data, taken at different temperatures, as shown in Table 1.
Table 1. Constants of exponential components of isothermal decay of H\textsuperscript{o} trapped in BABAL glass [33].

<table>
<thead>
<tr>
<th>a\textsubscript{1} (cm)</th>
<th>a\textsubscript{2}</th>
<th>a\textsubscript{3}</th>
<th>b\textsubscript{1} (10\textsuperscript{-3} min\textsuperscript{-1})</th>
<th>b\textsubscript{2}</th>
<th>b\textsubscript{3}</th>
<th>Annealing temp. (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>11.7</td>
<td>4.6</td>
<td>2.2</td>
<td>2.99</td>
<td>29.7</td>
<td>143</td>
<td>183</td>
</tr>
<tr>
<td>6.2</td>
<td>6.9</td>
<td>4.45</td>
<td>4.34</td>
<td>30.7</td>
<td>130</td>
<td>188</td>
</tr>
<tr>
<td>4.95</td>
<td>6.65</td>
<td>4.7</td>
<td>6.88</td>
<td>38.1</td>
<td>206</td>
<td>193</td>
</tr>
<tr>
<td>3.35</td>
<td>6.05</td>
<td>7.0</td>
<td>14.73</td>
<td>58.7</td>
<td>274</td>
<td>198</td>
</tr>
<tr>
<td>–</td>
<td>5.15</td>
<td>11.4</td>
<td>–</td>
<td>47.3</td>
<td>310</td>
<td>203</td>
</tr>
</tbody>
</table>

Applying the Arrhenius method, the following activation energies were obtained: E\textsubscript{1} = (0.32 ± 0.06), E\textsubscript{2} = (0.10 ± 0.02), and E\textsubscript{3} = (0.15 ± 0.02) eV.

In order to check the validity of the hypothesis that the Van der Waals interaction of H\textsuperscript{o} with the nearest neighbouring oxygen atoms of the BABAL glass matrix (see Fig. 3a), some preliminary calculations of Van der Waals interaction energies were carried out by assuming, as first approximation, that an atomic H\textsuperscript{o} is located at the center of a regular polygon or “ring structure” (see Fig. 3b) of oxygens occupying n vertices, known to exist in the structure of oxide glasses [1]. The results are tentatively correlated with the experimental activation energies, as shown in Table 2, where the agreement is quite acceptable, as expected for polygonal ring structures of 5, 6 and 7 corners, respectively.

The properties of H\textsuperscript{o} trapping sites of the oxide glass considered in the example above, and the neutral character of the atomic hydrogen, suggest that the Van der Waals forces are consistent as the stabilization mechanism of neutral atoms below room temperature. The other stabilizing mechanism of imprisonment in cages seems to be the only remaining alternative possible for neutral atomic centers stabilized at higher temperatures.

2.2. H\textsuperscript{o} trapped in a-Si:(N,O,H) [36,37]

For the H\textsuperscript{o} centers, stable above room temperature, the model of trapping sites of atomic hydrogen held by Van der Waals forces is no more valid. Thus the enclosure of the atoms in cages seems the only alternative hypothesis feasible to be considered. Similar method of kinetic studies from the previous example above was applied. The results were also compared with those of a H\textsuperscript{o} trapped in a crystalline sample of natural beryl [38] and pink tourmaline [39].

Fig. 3. (a) Two-dimensional schematic representation of the oxygen ring structures expected for a BABAL glass. (b) A neutral H\textsuperscript{o} center located at the center of a regular polygon of oxygens.
The isochronal decay of H° in a-Si[N,O,H] [36] vanishes at temperature as high as 370 K, the activation energy is $E_a = 0.56$ eV and the preexponential frequency factor is $\alpha_0 = 1.5 \times 10^9$ s$^{-1}$ [37]. The H° stability is also as high for two sites measured in beryl of $E_a = 0.42$ eV and $E_b = 1.51$ eV and preexponentials $\alpha_0 = 3.33 \times 10^6$ s$^{-1}$ and $\beta_0 = 3.5 \times 10^{18}$ s$^{-1}$, respectively. For pink tourmaline the H° activation energy $E_a = 1.1$ eV was reported [39]. The H° is absent in a-Si:H, X-irradiated at 77 K [36] and the presence of oxygen in a-Si:[N,O,H] was shown to be essential for the trapping of neutral hydrogen.

Among the EPR responses described for the X-irradiated a-Si:[N,O,H] [36], the silicon oxide E’ center was detected. This observation indicates the presence of SiO$_4$ tetrahedrons in the system. The EPR line shape of the H° in this particular matrix reveals that there are two kinds of trapping sites for the neutral hydrogen: the first one, a relatively empty cage, free of hydrogen-terminated silicon bonds, where the H° EPR narrow ($\Delta B = 1$ Oe) component is homogeneous. The second kind of H° sites is revealed by broad ($\Delta B = 15$ Oe) component of an heterogeneous line, indicating a strong dipole-dipole interaction. Another paramagnetic response has revealed the presence of oxygen-related, peroxyl radicals and/or O$_5$°. The H° homogeneous EPR component can be ascribed to a contribution of H° imprisoned inside na oxygen cluster and the remaining H° centers are trapped in cages between SiO$_4$ tetrahedrons and Si–H terminated bonds, as suggested by the presence of dipole-dipole broadening. However, more specific models are still required to be developed for an adequate description of these sites.

2.3. Stabilization of Ag° centers

The atomic Ag° has been widely studied by EPR, stabilized in several host matrices [25-32]. Previous work [32] has shown that the silver impurity ions interact strongly with radiation induced electron and hole centers in barium aluminoborate glasses. The kinetic results for the Ag° have shown that the isochnonal thermal decay of Ag° centers in barium aluminoborate glasses is different in nature from the H° centers trapped in the same glass matrix.

Unlike the H°, the Ag° center stability in borate glasses is extended to temperatures above room temperature, and the isochnonal decay vanishes at about 550 K. Clearly, after the Van der Waals binding forces are overcome by heating, the Ag° atoms still remain relatively stable, showing a similar behaviour of H° centers held into cages of neighbouring oxygen atoms. The Ag° and Ag$_2^+$ centers vanished at the same limiting temperature of 550 K, which is also the approximate limit for the boron oxygen-hole centers (BOHC), suggesting that the last electron-hole recombinations, previously scavenged by Ag° ions, can occur via the two possible reactions:

$$\text{Ag}^\circ + \text{Ag}^\circ \rightarrow 2 \text{Ag}^\circ$$

and

$$\text{Ag}^\circ + h^\circ_{\text{BOHC}} \rightarrow \text{Ag}^\circ$$

The activation energy of the reaction (1) is related to the diffusion of silver atoms in the glass, and for the reaction (2), the respective decay (1) is related to the diffusion of silver atoms in the glass, with activation energy equal to ~1.0 eV [43].
3. The distribution of bridging oxygen ring structures in oxide glasses

One remaining challenging question is that no direct experimental technique was not yet available to study the distribution of the number of irregular polygonal or “ring structures” of bridging oxygens in the oxide glass. In order to face this kind of problem, excellent methods of computer simulations are available [44], but the experimental data to confirm the results are still lacking.

From the kinetic studies of the H⁺ centers in borate glasses, it is suggested that the measurement of the stabilization energies, assumed to be of the Van der Waals type, is feasible to be applied directly in order to determine the distribution of oxygen ring structures in the amorphous glass lattice.

4. Conclusion

The stabilization mechanisms of paramagnetic neutral atomic centers in oxide glasses can be evaluated by kinetic measurements using EPR and classified in two major groups:

(a) neutral atoms held by means of Van der Waals forces close or inside polygonal arrays of bridging oxygens or “ring structures” of the glass forming lattice;

(b) neutral atoms enclosed in cages of neighbouring bridging and/or non-bridging oxygen atoms of the amorphous network.

The kinetic studies of H⁺ atomic centers of the group (a), stable for temperatures below 230 K, are perhaps the first approach to a direct experimental study of the distribution of the ring structures in oxide glasses.

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References