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The pressure-induced effects in the thermal equilibrium electron properties of semiconducting glasses

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Abstract. Strong pressure-induced effects in the thermal equilibrium properties of semiconducting glasses are revealed and theoretically analysed. The basic property under consideration is the concentration of the negative- U centres which determine the mobility-gap spectral structure and the related electron phenomena in the materials. For accessible high pressures, $10^4 \leq p \leq 10^5$ bar, a rapid increase of the concentration with growing pressure is predicted. This holds for ('weak') negative- U centres formed in typical, 'rigid', configurations for the vast majority of atoms, as both the mobility-gap width and the related effective magnitude of the negative pair-correlation energy decrease with pressure. However, at ambient (and low) pressure another type of centre, 'strong' negative- U centres formed in glassy atomic soft configurations, predominate, whose concentration decreases with increasing pressure. The resulting concentration of negative- U centres and some related characteristics are shown to exhibit a non-monotonic pressure dependence with a minimum. Future experimental tests of the corresponding theoretical relationships might determine the basic parameters of the phenomenon for the materials under consideration.

1. Introduction

The purpose of the present paper is to reveal and theoretically describe significant effects of accessible high pressure p ($\leq (1-3) \times 10^5$ bar) in electron properties of semiconducting glasses (SGs), for temperatures below the glass transition temperature T_g . In this connection it is worthy of note that, generally speaking, only very high, rather inaccessible, pressures, $p \geq 10^7$ bar, can give rise to strong transformations in the properties of crystalline materials (except for those in which pressure-induced phase transitions occur at lower critical pressures $p < 10^6$ bar, due to the existence of soft phonon modes) [1]. The situation in glasses in general is different: global transformations in their structure and properties (not necessarily phase transitions) may be expected at not very high pressures $p \approx 10^5$ bar, as a result of a kind of softness characteristic of a noticeable proportion of localized atomic motion modes (see below). In what follows, it is largely the pressure effects, affecting thermal equilibrium electron properties related to the mobility-gap states of the SGs, that are discussed.

As is well known, anomalous atomic dynamical phenomena are characteristic of glasses at ambient pressure; they are generally not observed for the corresponding crystals (see, e.g., [2, 3]). Low-temperature anomalies are observed in the thermal, dielectric, and acoustic properties of glasses, which are universal in these materials, and are considered to be due

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to extra types of low-energy excitation in the atomic dynamics. Moreover, anomalous electron properties (e.g., the coexistence of Fermi level pinning around the mobility-gap middle and of a very weak thermal equilibrium ESR signal) were observed for the SGs [4]. These properties have been attributed to anomalous charge carriers in the mobility gap, suggested to be singlet electron (hole) pairs of negative correlation energy U and of energy (per particle) around the Fermi level ζ : the so-called negative- U centres [2–4]. Both sets of anomalous properties can be theoretically described within a unified approach, the soft-configuration model, in which nanometric medium-range order (MRO) atomic configurations—soft configurations—of atomic concentration $c_a \approx 10^{-2}$ are characteristic of glasses [3]. Each soft configuration actually contains a single soft mode of motion (x) which generally exhibits anharmonic features. The soft modes determine the universal anomalous (compared to those of crystals) low-energy excitations in the atomic dynamics. Moreover, interactions of electrons (holes) in the mobility gap with the soft modes give rise to an anomalous type of extremely strong electron (hole) self-trapping, due to very large distortions in the soft modes, which differs substantially from the well-known polaronic self-trapping [3, 5]. Most of the soft configurations are (quasi)harmonic in the soft-mode displacements, as are the common ‘rigid’ local configurations in the essential atomic motion mode displacements (x):

$$V(x) \approx V_0(x) = A\eta x^2 \quad \text{for } |x| < 1 \quad (1.1)$$

with A the characteristic atomic elastic energy per mode of motion.

Small values of the random ‘softness’ parameter η , $0 < \eta \leq \eta^* \approx 0.1\text{--}0.2$, are related to the soft configurations, whereas $\eta \approx \eta_0 \cong 1$ corresponds to the common ‘rigid’ ones. Then the negative- U centres are characterized by a spectrum of self-trapping energies $W_j(\eta)$ (<0) for a single electron ($j = 1$) or a singlet electron pair ($j = 2$) and of the pair-correlation energy $U(\eta)$ (<0). In particular, polaron-type relations would hold:

$$W_2(\eta) \cong W_2^0(\eta) = -Q^2/A\eta = 4W_1^0(\eta) \cong 4W_1(\eta) \quad (1.2a)$$

and

$$U(\eta) \cong U^0(\eta) = -Q^2/2A\eta + U_d \quad (1.2b)$$

if the ‘bare’ electron gap state under self-trapping were actually not hybridized with the other gap states. In equations (1.2), Q stands for the electron–soft-mode coupling parameter, and U_d is the Hubbard energy in the localized bare state. However, the hybridization of the bare electron state with the valence-band states becomes crucial as the typical bare energy ε , originally near the conduction-band mobility edge E_c^* , approaches the valence-band mobility edge E_v^* during the self-trapping process. In fact, the expressions for $W_1(\eta)$ and $U(\eta)$ may significantly deviate from equations (1.2), as the strong influence of the hybridization prevents $U(\eta)$ from being positive when $U^0(\eta)$ becomes positive (i.e. $U(\eta)$ remains negative); however, no such influence is available for states originally doubly occupied, so in general $W_2(\eta) \cong W_2^0(\eta)$ [3, 5].

The negative- U centres under consideration actually determine, from this viewpoint, the gap-related electron properties of SGs observed at ambient pressure. The earlier models [2, 4] can be considered as limit cases of the soft-configuration-model theory [3, 5]. The thermal equilibrium concentration c_2 of the negative- U centres is related to their density of states (DOS) $g_2(E)$ at the single-particle Fermi level, $E = \zeta$, or to the bare single-particle DOS $g_0(E^*)$ at the corresponding mobility edge E^* ; e.g., for electrons at ambient pressure in SGs,

$$10^{-4} \leq c_{2e}(0) \approx g_0(E_c^*) w c_a(0) \leq 10^{-3} \quad (1.3)$$

for typical $g_0(E_c^*)$ and band-tail width w , i.e. with $10^{-2} \leq g_0(E_c^*)w \leq 10^{-1}$ (see, e.g., [2, 5]). Note that for ambient pressure the glass characteristics $X(p)$ are denoted as $X(0)$ —e.g., $c_a(0)$ and $E_g(0)$. The estimation (1.3) agrees with the basic data concerning the gap-related electron properties of the SGs at ambient pressure.

The problem under discussion is that of revealing and describing the basic pressure effects in thermal equilibrium electron properties of SGs, such as the specific heat $C^{(e)}$ and magnetic susceptibility $\chi_m^{(e)}$, which are largely determined by the pressure effects in the concentration c_{2e} of the electronic negative- U centres (e.g., $C^{(e)} \propto c_{2e}$). Moreover, in SGs, the intensities of (weakly) non-equilibrium processes $I_q^{(e)} \propto c_{2e}W_q^{(e)}$, with $W_q^{(e)}$ the corresponding transition probability. Thus, the pressure effects in I_q are also due to those in c_{2e} , rather than in W_q , as strong effects are characteristic of c_{2e} , for high pressures at least. An example is the contribution of thermal single-particle excitations of the negative- U centres to the d.c. conductivity, $\Delta\sigma_{dc}(T, p) \propto c_{2e}(p) \exp[-U_{eff}(p)/T]$, with $U_{eff}(p)$ the effective magnitude of the negative correlation energy.

Hence, we focus in the present paper on the concentration $c_{2e}(p)$ of the negative- U centres. In what follows, as well as above, electron negative- U centres are explicitly considered, the situation for hole ones being similar, with trivial substitutions.

The qualitative features of the model and the basic assumptions, as well as the estimations of the pressure dependence of the basic parameters of the theory, are described and analysed in section 2. The basic analytical expressions and approximations of the theory are presented in section 3. The results of analytical and numerical calculations for $c_{2e}(p)$ are given and discussed in section 4. The analysis is mainly concentrated on temperatures not too close to T_g and on high pressures in the semiconducting phase of the materials in question. In this connection it should be noted that the SG is characterized by the finite mobility-gap width $E_g(p)$ which decreases with growing pressure up to a global semiconductor–metal phase transition at $p = p_g$, with $E_g(p_g) = 0$ and $p_g \approx (1-2) \times 10^5$ bar [6–8]. Some conclusions are presented in section 5.

2. Qualitative features and basic assumptions of the model

At low pressures $p \ll p_g$, as well as at ambient pressure, for which $E_g(p) \cong E_g(0) \approx 2-3$ eV for SGs, the negative- U centres are formed due to the singlet-pair self-trapping under consideration, which occurs in the soft configurations (1.1). In fact, the hybridization of states becomes decisive as the bare electron energy is reduced during the self-trapping process by $\delta\varepsilon \approx W_2^0(\eta_g) = Q^2/A\eta \approx E_c^* - E_v^* = E_g(p)$. Then, the essential configuration ‘softness’ $\eta \approx \eta_g = Q^2/AE_g(p)$ mostly falls in the range $0 < \eta \approx \eta_g < \eta^*$ for $Q \approx 4-6$ eV and $A \approx 50-100$ eV, typical for SGs, and the effective magnitude $U_{eff}(p)$ of the negative correlation energy is large, $U_{eff}(p) \approx U_{eff}^0(p) \cong E_g(0)/2 \gg U_d$ for realistic values of U_d [3]. In this sense, the negative- U centres are defined as ‘strong’. However, negative- U centres can also be formed in typical ‘rigid’ configurations for $\eta^* \ll \eta \approx \eta_g \leq 1$ —in materials with ‘narrow’ gaps $E_g(0) \ll 1$ eV or in ‘wide’-gap materials (e.g., SGs) for $E_g(0) \geq 1$ eV, at high pressures with $E_g(p) \ll 1$ eV. The latter are defined as ‘weak’ negative- U centres, being characterized by small values of $U_{eff}(p) \approx E_g(p)/2 \ll 1$ eV. Negative- U centres of intermediate type are formed in intermediate local atomic configurations. Since the atomic concentration is $c_0 \cong 1$ for typical ‘rigid’ configurations, while it is much lower, $c_a(0) \approx 10^{-2}$, for the soft configurations, one can expect that the concentration of the (‘weak’) negative- U centres at high p , rather close to p_g , will be much higher than $c_{2e}(0)$, $10^{-4} \leq c_{2e}(0) \leq 10^{-3}$, for the ‘strong’ negative- U centres at ambient pressure. Furthermore, as argued below (see equation (2.3), and also [3,

9)), the concentration of the ‘strong’ negative- U centres in general decreases with growing pressure. Hence, the total concentration $c_{2e}(p)$ at first decreases with increasing p , and then increases at high enough pressure in SGs for $p < p_g$ and $T < T_g$. The relationships characterizing this basic pressure-induced effect predicted for SGs in the present paper are derived and analysed in section 4.

The basic parameters of the negative- U centres in the theory under consideration are the mobility-gap width $E_g(p)$ and the effective width $\Delta\eta$ of the distribution density $\aleph(\eta)$ for the local configuration ‘softness’ η .

As experimentally established, $E_g(p)$ decreases with increasing pressure to $E_g(p_g) = 0$, with the slope slightly varying [6, 7], which can be taken into account in numerical calculations. Then, $E_g(p)$ can be approximated (with corrections less than 10%) by

$$E_g(p) = E_g(0)(1 - \alpha_g p) \quad (2.1)$$

for $p < p_g \equiv \alpha_g^{-1}$.

The function $\aleph(\eta)$ can be approximated as follows [3]:

$$\aleph(\eta) = C_1(\eta)\eta_0^{-1} \exp[-\alpha(p)(1 - z)^2] \equiv C_1(\eta)\eta_0^{-1}\phi(z). \quad (2.2)$$

Here, $C_1(\eta)$ is a relatively slow function, $0 \leq C_1(\eta) \leq C_1(\eta_0)$, while $0 \leq z \equiv \eta/\eta_0 \leq 1$ and $\alpha(p) \equiv \eta_c^{-1}(p)$ at $\eta_c(p) \approx (\Delta\eta(p))^2$. The resulting atomic concentration in a glass (not too close to T_g)

$$c_a(p) = \int_0^{\eta^*} d\eta \aleph(\eta) \approx c_a(0) \exp(-\delta\alpha(p)) \quad (2.3)$$

is of the correct order of magnitude for $p = 0$, $c_a(0) \approx 10^{-2}$, at $\alpha(0) \cong 10$ and $C_1^0 \approx 10$. Moreover, $\delta\alpha(p) = \alpha(p) - \alpha(0)$ (>0) increases with pressure, so $c_a(p)$ decreases and the soft configurations are suppressed on the pressure scale p_η , $10^5 \text{ bar} \leq p_\eta < 10^6 \text{ bar}$ [3, 9]. This universal high-pressure phenomenon, due to the decrease of the width $\Delta\eta(p)$ of $\aleph(\eta)$ with growing p , is assumed to be rather well described in the approximation

$$\delta\alpha(p) = \alpha(p) - \alpha(0) \cong p/p_\alpha \quad \text{for } p_\alpha = p_\eta/\alpha(0) \quad (2.4)$$

for $p_\alpha \leq p \leq p_\eta$ at least. In fact the soft-configuration suppression, ultimately related to the densification of the material, is strongest for the above-noted accessible high pressures [9]. It follows from the above that the concentration of the ‘strong’ negative- U centres, basically related to the soft configurations, also decreases with pressure, $c_{2e}(p) \cong c_{2e}(0) \exp(-\delta\alpha(p))$ (see equation (1.2)).

It is worth adding that a global transformation (not necessarily a phase transition; cf. [10]) was observed in the elastic properties of amorphous semiconductors on increasing the average coordination number z_{av} from $z_{av} < z_c$ (SGs), for $2.67 < z_c < 3$, to $z_{av} > z_c$ (e.g., $z_{av} = 4$ for a-Si). Moreover, one could also expect such a transformation in a given SG with pressure increasing from $p \ll p_\eta$ to $p \geq p_\eta$, as long as z_{av} was observed to increase with p , for $dz_{av}/dp \leq 10^{-5} \text{ bar}^{-1}$ [6]. Since, however, no such global transformation was detected in SGs for $p < p_g$, one may conclude that $p_g \leq p_\eta$ (see also [9]).

We should note that all of the other parameters of the theory ($Q = Q_{c,v}, U_d = U_d^{(e,h)}, A, w$; see equations (1.1)–(1.3)) can be approximated for actual $p < p_g$ as being independent of p . In fact, in the SGs, due to the chalcogen atom chemistry (the existence of lone pairs) [11],

$$dE_g/dp = dE_v^*/dp = dD_v/dp \gg dE_c^*/dp = dD_c/dp \quad (2.5)$$

so the scale $p_{c,v}$ of variations of $Q_{c,v}$ with growing pressure can be estimated as follows:

$$|p_c| > |p_v| \approx p_g D_v(p=0)/E_g(p=0) \approx 3p_g \gg p_g \quad (2.6)$$

and $Q_{c,v}(p) \cong Q_{c,v}(0)$ for $p < p_g$ ($D_{c,v}$ stands for the corresponding band width). Since $D_{c,v}$ is determined by the corresponding ‘site’ wave-function overlaps, it should be substantially more sensitive to pressure than ‘site’ characteristics, such as U_d , so one can assume that also $U_d(p) \cong U_d(0)$ for $p < p_g$. The typical atomic elastic energy $A \equiv k_0 a_0^2 / 2 = M_0 \omega_0 a_0^2 / 2$, with k_0 , M_0 , and ω_0 the typical values of the spring constants, atomic mass, and vibration frequency, and a_0 the atomic length scale ($a_0 \cong 1 \text{ \AA}$), so $dA/dp = 2A \, d\ln(\omega_0)/dp$. Since $c_a \approx 10^{-2}$ and for the vast majority of atoms $d\ln(\omega_0)/dp \leq 10^{-6} \text{ bar}^{-1}$ in a solid [12], it appears that it is indeed the case that $A(p) \cong A(0)$ for $p < p_g$. The band-tail width w is generally considered as a measure of the degree of disorder in the materials in question. The degree of disorder is not expected to diminish under high pressure. The latter appears to affect the glass structure by destroying [3, 9] its atomic medium-range-order configurations [13] (equation (2.3)). Therefore, increasing pressure is not expected to decrease w , and it is assumed that $w(p) \cong w(0)$ for $p < p_g$.

3. Basic relations and approximations

The basic relation applied here for calculating $c_{2e}(T, p)$ is as follows:

$$c_{2e}(T, p) = \int_0^{E_g(p)} d\varepsilon g_0(\varepsilon) \int_0^{H(p)} d\eta \aleph(\eta) \Phi_e^{(2)}(\varepsilon; \eta) \quad (3.1)$$

with $H(p) \cong \{\eta^* \text{ for } p \ll p_g; \eta_0 \text{ for } 0 < p_g - p \ll p_g\}$. Here the bare density of states (DOS) $g_0(\varepsilon)$ rapidly decreases as ε drops away from E_c^* into the mobility gap (see, e.g., [4]):

$$g_0(\varepsilon) = g_0 \exp[-((E_g - \varepsilon)/w)^\mu] \quad (3.2)$$

where in fact $1 \leq \mu \leq 2$. The bare energy ε is referred to the valence-band mobility edge, $E_v^* = 0$, so $0 \leq \varepsilon \leq E_c^* = E_g$, and $g_0 \equiv g_0(E_c^*) \approx (1/3)D_0$ for $D_0 \approx Q \approx 4\text{--}6 \text{ eV}$ and $2w \approx 0.1 D_0$ for SGs. As usual, the Gibbs pair occupation

$$\Phi_e^{(2)}(\varepsilon; \eta) = \exp(X_{2e})/Z_e \cong \{1 + \exp((E_{2e} - \zeta)/k_B T)\}^{-1} \equiv f_F[E_{2e}(\varepsilon; \eta) - 2\zeta] \quad (3.3)$$

where $Z_e = 1 + 2 \exp(X_{1e}) + \exp(X_{2e})$ and $X_j = (j\zeta - E_{je}(\varepsilon; \eta))/k_B T$ for the bare energy level (ε) nominally occupied by j electrons, with the energy E_{je} of j self-trapped electrons and the Fermi level ζ (per particle) referred to the energy of the empty state ($E_{0e} = 0$ at $j = 0$) and to the valence-band mobility edge, respectively. For the system under discussion for which the negative- U centres correspond to the ground state, $\Phi_e^{(2)} \gg \Phi_e^{(1)}$ and $\Phi_e^{(2)}(\varepsilon; \eta) \cong \theta(2\zeta - E_{2e}(\varepsilon; \eta))$ for low enough $T \ll T_{eff}^0$ (equation (3.5)), while $f_F(E_{2e} - 2\zeta)$ is the Fermi-like distribution related to the step function $\theta(2\zeta - E_{2e})$ for the singlet electron-pair energies.

In fact, focusing in what follows on calculations and the analysis of $c_2(T, p) \cong c_2(0, p) \equiv c_2(p)$ for low enough $T \ll T_{eff}^0$, one may straightforwardly transform equation (3.1) to the following expression:

$$c_{2e}(T, p) \cong \int_0^{E_g(p)} d\varepsilon g_0(\varepsilon) L_2(\varepsilon; p) \quad (3.4)$$

$$L_2(\varepsilon; p) = \int_0^{H(p)} d\eta \aleph(\eta) f_F(E_{2e}(\varepsilon; \eta) - 2\zeta).$$

Here

$$E_{2e}(\varepsilon; \eta) = 2\varepsilon + U_d + W_{2e}(\eta)$$

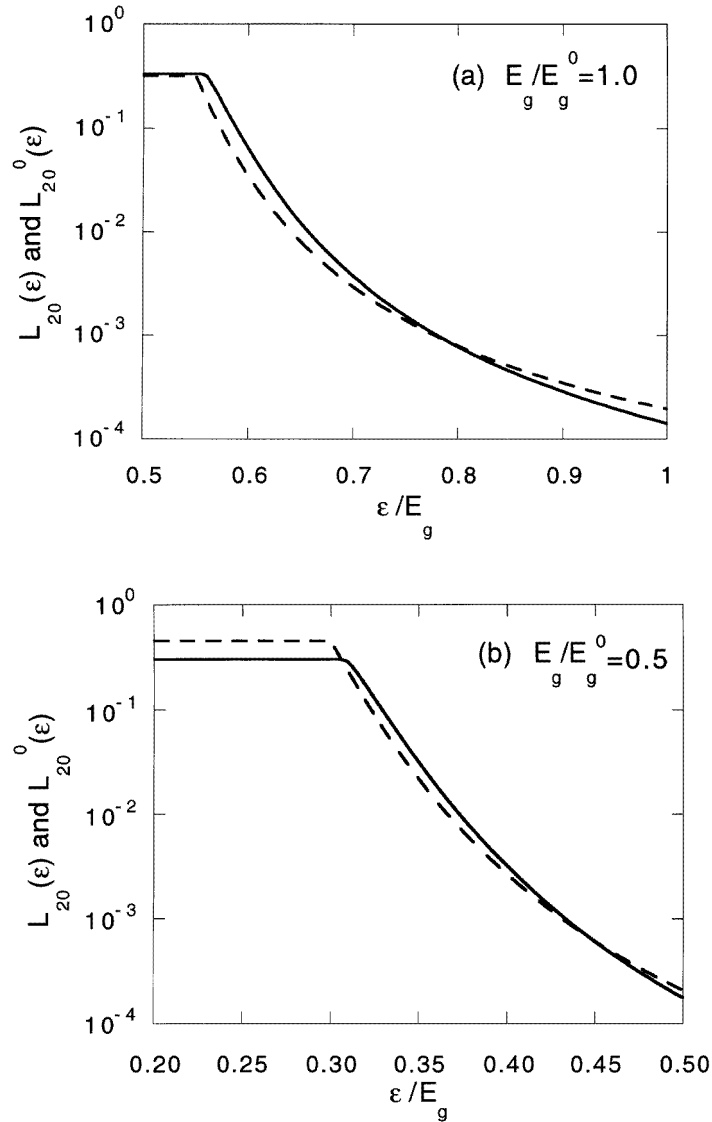


Figure 1. The dependence on the bare energies of the integral L_2 in equation (3.4) at $T = 0$ (solid line) and of its theorem-on-average approximation given as equation (3.8) (dashed line) at: (a) $\gamma^0 = 0.65$ and $E_g = E_g(0) = 1$; (b) $\gamma^0 = 0.75$ and $E_g = 0.50$; (c) $\gamma^0 = 0.77$ and $E = 0.20$. The main set of the parameter values is as follows: $\gamma^* = Q^2/A\eta_0 = 0.2$ (equation (3.5)), $\alpha(0) = 10$, and $p_g/p_\eta = 1$ (equations (2.2)–(2.4)).

and

$$W_{2e}(\eta) = W_{2e}^0(\eta) = -\gamma^* \eta_0 / \eta$$

for $\gamma^* \equiv Q^2/A\eta_0$. As usual in Fermi–Dirac statistics, the low-temperature estimation of $L_2(\varepsilon)$ can be performed by expanding $\Phi_e^{(2)}(\varepsilon; \eta) = f_F[E_{2e}(\varepsilon; \eta) - 2\zeta]$ in powers of T , the first term corresponding to the Fermi step function $\theta[2\zeta - E_{2e}(\varepsilon; \eta)]$. In fact

$$L_2 = L_{20} + \Delta L_2 \quad (3.5)$$

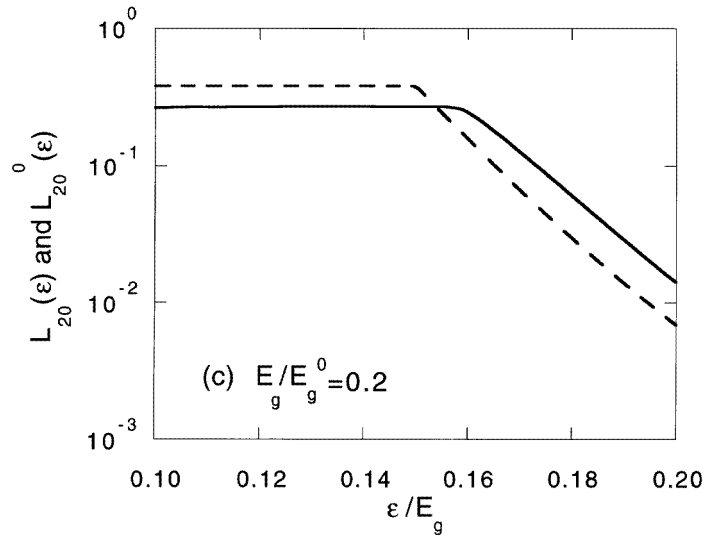


Figure 1. (Continued)

where

$$L_{20} \equiv L_{2|T=0} \quad \text{and} \quad |(\Delta L_{20}/L_{20})| = d_1(T/T_{eff})^2 + d_2(T/T_{eff})^4 + \dots$$

for $d_1 \approx 1 \approx d_2$ with accuracy to an exponentially small correction: $|\delta_2| < (T/T_{eff}) \exp[-(T_{eff}/T)]$ at $q = (\gamma^*/k_B T_{eff})^{1/2} \leq 1$ for typical $\gamma^* = Q^2/A\eta_0 \cong 0.2E_g(0) \gg k_B T_g$ and $T < T_{eff}$. Note also that the electroneutrality equation $c_{2e}(\zeta) = c_{2h}(\zeta)$ for the negative- U centres in the intrinsic SGs, for low $T \ll T_{eff}$ and $k_B T \ll E_g/2$, gives rise to [5]

$$2\zeta \cong E_g. \quad (3.6)$$

It follows from equations (2.2), (3.4)–(3.6) that for $T \ll T_{eff}$ and $k_B T \ll E_g/2$

$$L_{20}(\epsilon) \cong L_{20}(\epsilon) = \aleph_0[\eta_0 \sqrt{\pi/2} \sqrt{\alpha(p)}][\Phi(t_{max}) - \Phi(t_{min})] \quad (3.7)$$

where $\aleph_0 \eta_0 \approx C_1(\eta_0)$, $0 < t_{min} = t_{max}(1 - z_{max}(\epsilon)) < t_{max} = \sqrt{\alpha(p)}$ for typical $\alpha(p) \geq 10$, and $\Phi(t)$ is the probability error integral, while $1 \geq z_{max}(\epsilon) = \eta_{max}(\epsilon)/\eta_0 = \gamma^*/(2\epsilon - E_g + U_d) > 0$.

In accord with the limits of equation (3.7) for $z_{max} \rightarrow 0$ and $z_{max} \rightarrow 1$, a reasonable analytical estimate of $L_{20}(\epsilon)$ can be obtained by applying the theorem on average, as the integrand and its derivatives monotonically increase with growing z , from $z = 0$ to z_{max} , and the main contribution is due to an appropriate average z^0 rather close to z_{max} . The result is that

$$L_{20}(\epsilon) = \gamma_1 \aleph_0 z^0 \Phi(z^0) \quad (3.8)$$

where $z^0 = \gamma^0 z_{max}(\epsilon)$ at $\gamma^0 \cong 1 \cong \gamma_1$. It follows from numerical calculations (figure 1) that the approximation (3.8) is reasonable (with accuracy to small corrections not exceeding $\approx 10\%$) for $\gamma^0 \approx 0.65$ – 0.75 for $1 \geq E_g/E_g(0) \geq 0.1$ and a typical set of values of the other parameters, e.g., $\gamma^* = Q^2/A\eta_0 \cong 0.2E_g(0)$ and $U_d \cong 0.1E_g(0)$.

The standard procedure of Fermi integral calculation gives rise to the following estimation of $T_{eff}^0(p) \equiv T_{eff}(\epsilon_{max})$ for the bare energies $\epsilon = \epsilon_{max} = \gamma_0 E_g(p)$ for $\gamma_0 \cong 1$,

giving the major contribution to the integral in equation (3.4) (see [5], and table 1, in section 4):

$$k_B T_{eff}^0(p) \equiv k_B T_{eff}(\varepsilon_{max}) \cong \gamma^*/z_{max}^{\kappa}(\varepsilon_{max}) = (\gamma^*)^{1-\kappa}(\varepsilon_{max} + U_d)^{\kappa} \quad (3.9)$$

with $\kappa \approx 2$ and $z_{max}(\varepsilon_{max}) \equiv z_{eff}(p) = \gamma^*(\gamma_0 E_g(p) + U_d)^{-1}$, and hence $T_{eff}^0(0) \geq 10\gamma^* \geq 10^4$ K $\gg T_{eff}^0(p_g) \approx T_{eff}^0(0)(U_d/E_g(0))^{\kappa} \geq 300$ K for the actual values $E_g(0) \approx 2-3$ eV $\approx 5\gamma^* \geq 10U_d$. Then, for SGs,

$$T \ll T_{eff}^0(p) \quad \text{and} \quad k_B T \ll E_g(p)/2 \quad \text{for } T < T_g \quad (3.10)$$

at least at pressures not too close to p_g at which the semiconductor–metal transition occurs.

One may conclude that the temperature effects in the concentration of the negative- U centres are indeed weak:

$$c_{2e}(T, p) \cong c_{2e}(0, p) \equiv c_{2e}(p) \quad (3.11)$$

over the glass range below T_g , or over most of it.

Eventually, the analytic approximation (3.1), for the relatively low temperatures given in (3.10), gives rise to the expression

$$c_{2e}(p) \approx \aleph_0 \int_0^{E_g(p)} d\varepsilon g_0(\varepsilon) \Phi[z^0(\varepsilon)] z^0(\varepsilon). \quad (3.12)$$

4. The pressure dependence of the concentration of negative- U centres

In what follows the main results of the analytical and numerical calculations of equation (3.12) are presented and analysed; they predict the non-monotonic pressure dependence of the concentration $c_{2e}(p)$ of the negative- U centres discussed qualitatively in section 2.

The standard rapid decrease of the bare DOS $g_0(\varepsilon)$ in the mobility gap (equation (3.2)) strongly favours $\gamma_0 = \varepsilon_{max}/E_g = 1$, as if the main contribution to the integral in equation (3.12) is due to $\varepsilon \cong E_g(p)$. However, the energy dependence of $z_{max}(\varepsilon)\phi(z_{max}(\varepsilon))$ in the integral may give rise to a deviation of γ_0 from unity, which has to be estimated from analytical and numerical calculations. It follows from equations (3.2), (3.7), and (3.12) that

$$c_{2e}(p) \approx g_0 \aleph_0 \gamma^* J(p; \mu) \quad (4.1)$$

$$J(p; \mu) = \int_{y_m(p)}^{y_g(p)} dy f(y; \mu) \quad (4.2)$$

where $f(y; \mu) = \exp[\Phi(y; \mu)]$, $\Phi(y; \mu) = -\alpha(p)y^2 - \psi(y; \mu) - \ln(1-y)$, and $\psi(y; \mu) = [\beta(y_g - y)/(1-y)(1-y_g)]^{\mu}$, for $\beta = \gamma^*\gamma^0/2w \approx 1$, for the typical values $\gamma^* \approx (0.1-0.2)E_g(0)$ and $2w \approx 0.1D_0$.

Moreover, $y = y(\varepsilon) \equiv 1 - \gamma^0 z_{max}(\varepsilon) < 1$, for $z_{max}(\varepsilon) > 0$, and $dy/d\varepsilon < 0$, so $1 > y_g(p) \equiv y(E_g(p)) > y_m(p) \equiv y(\varepsilon_m(p))$ for $E_g(p) > \varepsilon_m(p)$.

In accordance with the expression for $z_{max}(\varepsilon)$ in equation (3.7),

$$\varepsilon_m(p) = (E_g(p) - U_d)/2 \quad \text{and} \quad y_m(p) = -\infty \quad (4.3)$$

for pressure that is not too high, $p < p_u = p_g(1 - U_d/E_g(0))$, for

$$E_g(0) \geq E_g(p) > U_d. \quad (4.4)$$

However, $\varepsilon_m(p) = 0$, so all energies $\varepsilon \geq 0$ contribute to $J(p; \mu)$ in the alternative case of the limit high pressure, $p_u \leq p < p_g$, for

$$U_d \geq E_g(p) \geq \varepsilon \geq 0 \quad \text{and} \quad y_m(p) < y_g(p) < 0 \quad (4.5)$$

at least for the actual values $\gamma^*\gamma^0 \geq 0.1E_g(0) \geq U_d$ implied below. Let us recall that the hybridization of states prevents the transformation of the negative- U centres to positive- U ones even at the limit high pressures (4.5) at which such a transformation would occur for hybridization-free bipolarons (equation (1.2)). The reason for this is that the hybridization of states gives rise to double occupation of the bare gap states by singlet pairs of valence-band electrons, strongly favouring the formation of the negative- U centres [3, 5].

Then, equation (4.2) can be presented as follows:

$$J(p; \mu) = J_+^{(\mu)}(p; y_g) + J_-^{(\mu)}(p; y_m) \tag{4.6}$$

$$J_{\pm}^{(\mu)}(p; a) \equiv \int_0^a dy f(\pm y; \mu).$$

Note that $y_g(p) \geq 0$ for $p \leq p_0 = p_g(1 + U_d/E_g(0) - \gamma^*\gamma^0/E_g(0))$, though $y_g(p) < 0$ for $p_0 < p < p_u$ for $p_0 < p_u$, in the case (4.4), whereas only $y_g(p) < 0$ for $p_g > p \geq p_u$, in the case (4.5). This holds in accordance with equation (3.9), as the effective configuration ‘softness’ $\eta_{eff}(p)$ does not exceed the characteristic value η_0 (equation (2.2)) for $p \leq p_0 < p_g$, for the actual values $\gamma^*\gamma^0 > U_d$ mentioned above.

The formulae (4.1)–(4.3) and (4.6) characterize $c_{2e}(p)$ for $p < p_g$, and may be applied for the following calculations and discussion. As seen from the function $\psi(y; \mu)$ being only dependent on μ , the features of $c_{2e}(p)$ are expected to be weakly sensitive to variations of μ , in the actual range $1 \leq \mu \leq 2$ at least. Hence, as a typical example, the pressure effects in $c_{2e}(p)$ are discussed for $\mu = 2$ (and μ is omitted below).

Table 1. The positions of the maximum ε_{max} of L_{20} for different gap widths E_g .

E_g	1.0	0.9	0.8	0.7	0.6	0.5	0.4	0.3	0.2	0.1
ε_{max}	1.0	0.88	0.78	0.68	0.58	0.47	0.35	0.22	0.16	0.10

Standard calculations for $1 \geq E_g(p)/E_g(0) \geq 0.10$ show that $f(y)$ exhibits a pronounced maximum at $y = M[p] \equiv M(E_g(p); \alpha(0), \beta)$ with a comparable width

$$\Delta_M = |d^2\Phi/dy^2|_M^{-1/2} \geq \alpha^{-1/2} \tag{4.7}$$

in the neighbourhood of $y_g(p)$. For instance, $M \cong 0.79$ for $1 \geq E_g(p)/E_g(0) > 0.8$ ($y_g \cong 0.95$), while $M \cong 0.75$ for $0.8 \geq E_g(p)/E_g(0) \geq 0.2$ ($y_g \approx 0.93$ – 0.84). In accord with the corresponding numerical calculations (table 1), the ratio $\gamma_0 = \varepsilon_{max}/E_g$ is indeed found to be close to unity, and so equation (3.9) is relevant. This holds particularly for not very small $E_g(p)/E_g(0) > 0.4$ with deviations less than 10%, whereas the deviations are less than or about 25% for $E_g(p)/E_g(0) \leq 0.4$.

Similarly to equation (3.8), the expression for $J_+(p; y_g)$ is approximated as

$$J_+(p; y_g) \approx y_g(p) \exp[\Phi(y_0)] = (y_g(p)/(-y_0(p))) \exp\{-\alpha(p)y^{-2}(p) - \psi(y_0; p)\} \tag{4.8}$$

for $y_0(p) = \lambda_0 y_g(p)$ and $\lambda_0 \cong 1$, corresponding to γ_0 rather close to unity. Moreover, the faster $g_0(\varepsilon)$ decreases in the gap (i.e., the larger μ), the closer λ_0 and γ_0 are to unity. Then, one can expect that $J_+(p; y_g)$ varies non-monotonically with pressure: increasing p gives rise to a decrease of $y_g(p)$ and of $y_0(p)$ while it gives rise to an increase of $\alpha(p)$ (equation (2.4)), so $J_+(p; y_g)$ is suggested to exhibit a minimum in the range $0 \leq p < p_g$ (note that $\phi(y_0(p)) = 0$ at $\lambda_0 = 1$). On the other hand, low $\varepsilon \approx 0$ give the major contribution to $J_-(p; y_m)$, which thus varies more weakly than $J_+(p; y_g)$ with growing pressure. Then, the suggested minimum of $c_{2e}(p)$ for $p = p_{min} < p_g$ can be estimated from the equation

$$dc_{2e}(p)/dp = 0 \cong d[-\alpha(p)y_g^2(p)]/dp \tag{4.9}$$

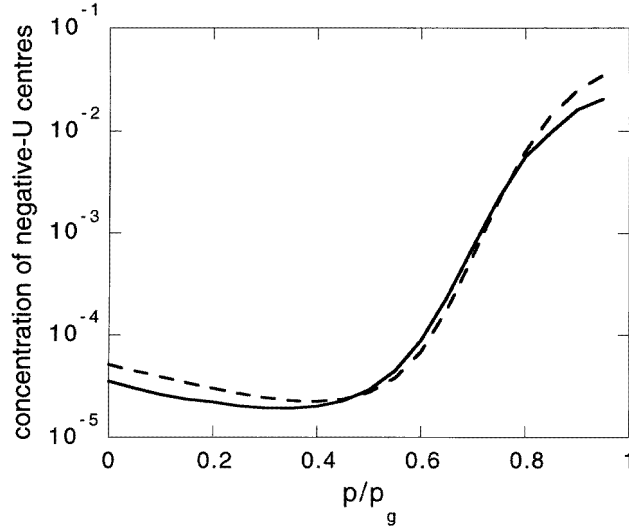


Figure 2. The pressure dependence of $c_{2e}(p) = c_{2e}(T = 0, p)$ from equations (3.5) and (3.8) (solid line) and from equations (3.12) and (4.1)–(4.2) (dashed line), for $\beta = 1$ and the same set of other parameter values as for figure 1.

at $p = p_{min}^0$, in the reasonable approximation in which the variations of $J(p)$ are mainly due to those of the exponential in equation (4.8). In equation (4.9), p_{min}^0 stands for the upper limit p_{min} , because the neglected lesser contributions to $J(p)$ give rise to an increase of $c_{2e}(p)$ and so to $p_{min} \leq p_{min}^0$. The resulting expression

$$v \equiv p_{min}^0/p_g \cong p_0/p_g - (2\gamma^*\gamma^0 p_\eta/E_g(0)p_g)^{1/2} \quad (4.10)$$

for $0 < v < 1$, e.g., $v \cong 0.45$ for $p_0/p_g < 1$ for the actual value $\gamma^*\gamma^0/E_g(0) \approx 0.2$, is the relevant root of the equation

$$v^2 - 2bv + c = 0$$

for

$$b = p_0/p_g + 3\gamma^*\gamma^0/2E_g(0) \quad \text{and} \quad c = (p_0/p_g)^2 - 2\gamma^*\gamma^0 p_\eta/E_g(0)p_g$$

for realistic values of p_g/p_η , $1 \geq p_g/p_\eta \geq 0.5$ (see section 2). As also expected qualitatively, p_{min}^0 grows with increasing p_g/p_η : $\alpha(p) \cong \alpha(0)$ for $p < p_g$ for small enough p_g/p_η , so practically $J(p)$ in general increases with increasing p (i.e., with decreasing $y_g(p)$). The results of numerical calculations for $c_{2e}(p)$, presented in figure 2 for the realistic set of parameter values noted, confirm the relevance of, and make specific, the above estimations:

$$p_{min} \cong 0.35p_g < p_{min}^0 \cong 0.45p_g \quad (4.11)$$

where p_{min} and p_{min}^0 are of the same order. Moreover, as seen from figure 2, the concentration $c_{2e}(p)$ of the ‘weak’ negative- U centres at the limit high pressure, $0.9 \leq p/p_g < 1$, is shown to be very high, $10^{-2} \leq c_{2e}(p) \leq 10^{-1}$, much higher than $c_{2e}(0)$, $10^{-4} \leq c_{2e}(0) \leq 10^{-3}$, for the ‘strong’ negative- U centres at ambient pressure. This prediction agrees with the qualitative features of the model in question as described

in section 2. Indeed, the estimation (1.3) may be extended to the limit of high pressures as follows:

$$c_{2e}(p) \approx g_0(E_c^*) w c_0(p) \approx 10^{-2} - 10^{-1} \quad (4.12)$$

with $c_0(p) \cong 1$. It is taken into account here also that both $\gamma_0(E_c^*)$ and w , as well as the band width D_0 (unlike the gap width), depend only weakly on p for $p < p_g$, in accordance with section 2. Relevant experimental data for comparison to the prediction under discussion could be obtained from measurements of the thermal equilibrium electron properties, e.g., the electron part of the specific heat of the SGs at low temperatures, which do not yet appear to have been made.

Two basic effects and their competition appear to determine the non-monotonic behaviour of $c_{2e}(p)$ with increasing pressure.

(i) The distribution density $\aleph(\eta)$ is narrowed, its width $\Delta\eta(p)$ decreasing with growing densification of the glass for $T = \text{constant}$ (see equation (2.4)), so the effective atomic concentration of the localized soft modes, related to the strong self-trapping in question, decreases. This effect will suppress the universal low-temperature properties of glasses, and may result in a continuous (though possibly rather sharp) transformation of the glass structure, for high pressure: $p \geq p_\eta \geq p_g$ (see also [9]).

(ii) The effective ‘softness’ $\eta_{eff}(p)$ of the local atomic configurations, participating in the pair self-trapping, increases with growing pressure. Since the distribution density $\aleph(\eta)$ increases with growing η (for $0 < \eta < 1$), the concentration $c_{2e}(p)$ of the negative- U centres also increases, whereas the pair-correlation energy $U(\eta_{eff})$, remaining negative, becomes small in magnitude: $U_{eff} = |U(\eta_{eff})| \approx E_g(p)/2$, compared to $E_g(0)/2$, so the self-trapping in this sense becomes weak. In fact, negative- U centres in SGs under high pressure can be created due to the self-trapping in question, even in typical ‘rigid’ configurations for $\eta_{eff}(p) \approx \eta_{eff}(p_0) = \eta_0 = 1$ (and $p_0 \leq p < p_g$), as long as $E_g(p)$ becomes so small that the pair self-trapping energy $W_2(\eta_0)$ (equations (1.2)) is comparable to $E_g(p)$. As noted above, this type of self-trapping (strong at $p = 0$) is due to the hybridization of states in the gap, which prevents the decay of the negative- U centres into positive- U ones.

5. Concluding remarks

The basic relationships characterizing the strong high-pressure effects in the thermal equilibrium electron properties of semiconducting glasses, associated with the negative- U centres in the mobility gap, are derived and analysed in the present paper. Analytical approximations and estimations, as well as the related results of the numerical calculations, are presented for the concentration $c_2(p)$ of the negative- U centres, for T and p not too close to T_g and p_g respectively—in fact, for $T < T_{eff}^0$ and $2k_B T \ll E_g(p)$. In this temperature range the temperature effects are weak while the effects of pressure tend to become strong. The most important effect of pressure is the predicted non-monotonic behaviour of $c_2(p)$ with increasing pressure, including the strong increase at high pressure and the pronounced minimum at $p = p_{min}$ which is of the same order as p_g , but not too close to it. The origin of the pressure effects is inherently related to the hybridization of states (decisive for the formation of the negative- U centres) and to two other fundamental properties of the SG. One of them is the suppression of the glassy soft modes of motion occurring because of the general densification of the glass at high pressure (with $T = \text{constant}$) [9]. Another property in question is the monotonic decrease of the gap width E_g with pressure from the substantial

value $E_g(0) \approx 2\text{--}3$ eV at ambient pressure down to $E_g = 0$ for $p = p_g \approx 10^5$ bar at which the global semiconductor–metal transition occurs [6–8]. Future experimental tests of the theoretical relationships for $c_2(p)$ at $p_{min} < p < p_g$, and for p_{min}/p_g , might determine the basic parameters $\eta_c(p)$ and p_η/p_g (in equations (2.3) and (2.4)) for the materials in question.

We would also like to mention a few other effects at high pressure close to p_g :

(i) the increase of the concentration $c_1(p)$ of the positive- U centres with growing pressure [9];

(ii) the substantial increase of the overlap of the negative- U centres for $p \rightarrow p_g$, which can develop into the Anderson–Mott delocalization of the charge carriers around the Fermi level in the gap [14]; and

(iii) the related low-temperature effects, such as the quasimetallic conductivity and the superconductivity in the SG even for $p < p_g$ (cf. the non-standard superconductivity observed in the SGs for $T \leq 10$ K and $p \sim 10^5$ bar) [8].

These and some other effects which follow from, and could compete to some extent with, the basic effects considered in the present paper, at the limit of high pressures p close to p_g , are to be discussed elsewhere.

To conclude, the materials under high pressure in question acquire new thermal equilibrium electron (as well as dynamic) properties, at least when relevant long-lived metastable (or polyamorphic [15]) ‘phases’ are produced.

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