«Диэлектрическая катастрофа» и переход диэлектрик-проводник

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Introduction

The **Clausius-Mossotti formula** for the dielectric constant ε of a perfect, homogeneous and isotropic dielectric

$$\varepsilon(n) = \frac{1 + 2b(n)}{1 - b(n)}, \quad b(n) = \frac{4\pi}{3}\alpha n$$

$b < 1$ is the refractivity, n is the density and α is the polarizability

The **Goldhammer-Herzfeld criterion** of the dielectric-conductor transition: $b \to 1$ or $\varepsilon \to \infty$ ("dielectric catastrophe")

D.A. Goldhammer, *Dispersion und Absorption des Lichtes in ruhenden isotropen Koerpern; Theorie undihre Folerungen*, Teubner, Leipzig, Berlin, 1913.
K.F. Herzfeld, *On atomic properties which make an element a metal.* Phys. Rev. 29, 701 (1927).

Dielectric-metal transition in doped semiconductors
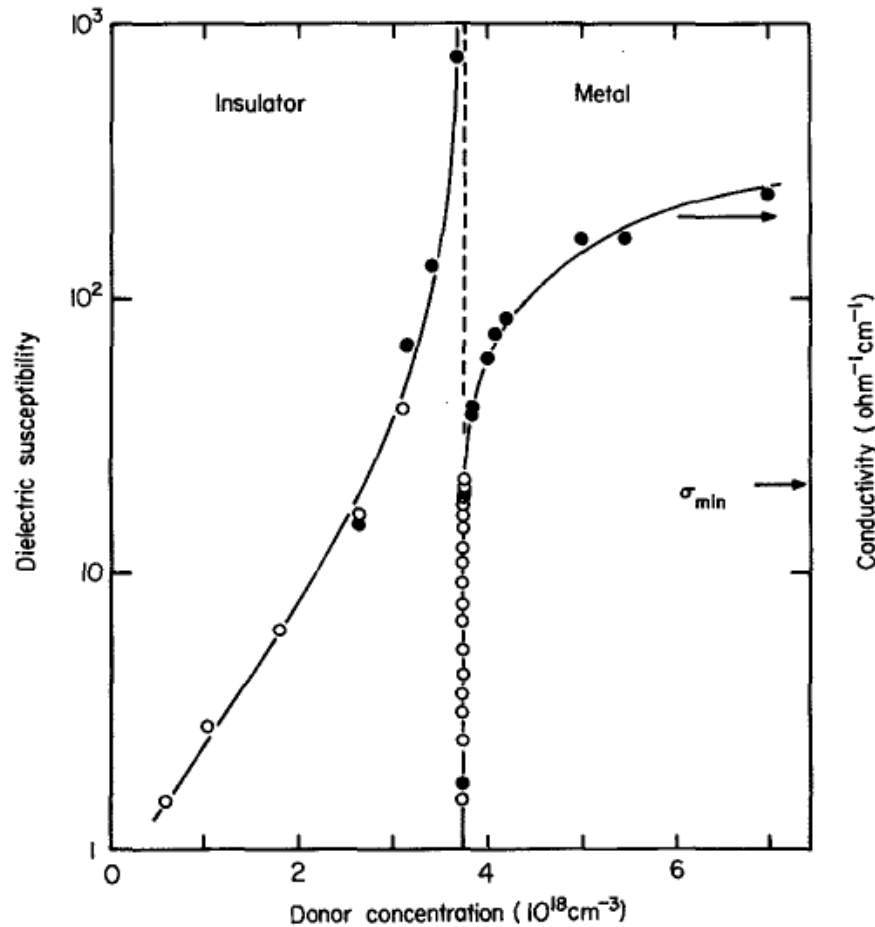

System - P:Si.

Phosphorus is donor.

Silicon is acceptor.

Hess *et al*., Phys. Rev. (1982)

Metal hydrides

Metal hydrides at ambient conditions are good dielectrics with large hydrogen content. It was suggested by Ashcroft (2004) that as a result of ``chemical precompression'' conductive state of metal hydrides could arise under significantly smaller pressures, than they are in case of pure hydrogen.

Stars – hydrogen

Squares – alane
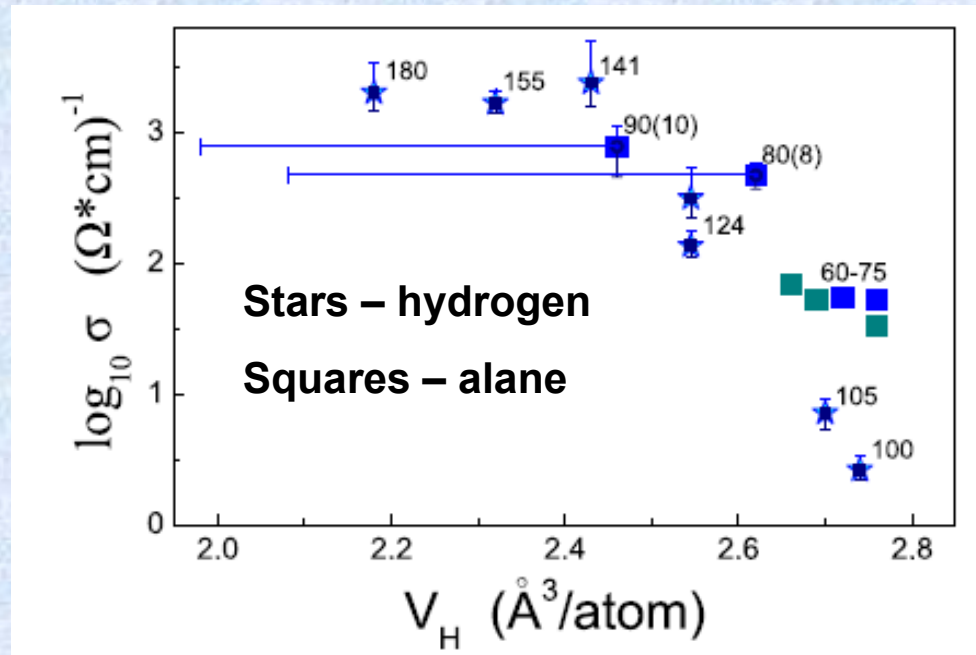
Recently, the metallization of alane (aluminum hydride) has been investigated. A stable metallic phase was found in low temperature static measurements at pressures above 100 GPa (Goncharenko et al. 2008). In multiple-shock compression experiments the dielectric-conductor transition has been observed at pressures about 80-90 GPa and temperature 1500-2000 K (Molodets09). In both experiments the density of molecules AlH_3, where the dielectric-conductor transition occurred, was about $5.6 \cdot 10^{22}$ cm^{-3}.

Polarizability of condensed alane

Polarizability of alane is unknown even in vacuum. For crude estimation one can use so called additivity rule (Shannon 1993)
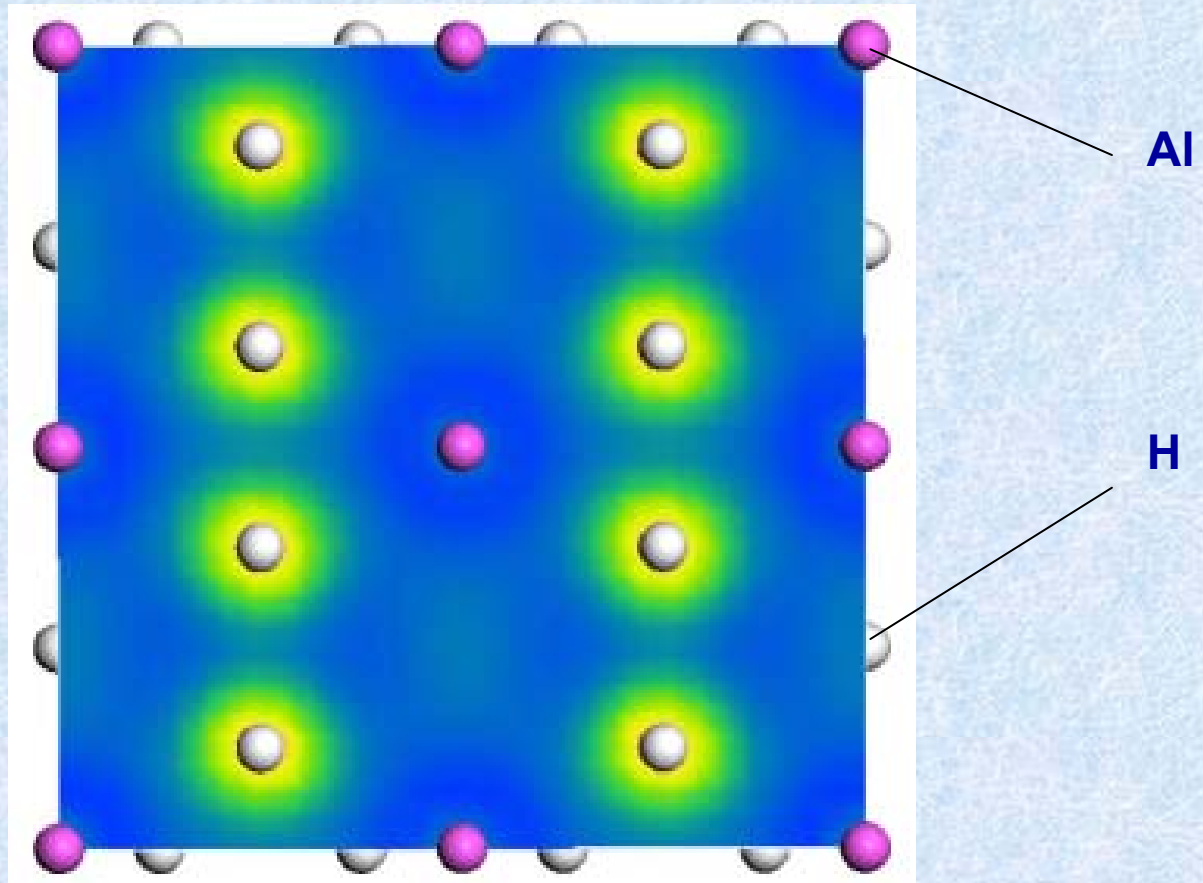
$$\alpha_{AlH_3} = \alpha_{Al} + 3\alpha_H$$

Polarizabilities of Al and H are equal to 56 and 4.5 a.u., correspondingly. This gives at ambient conditions $\alpha = 69.5$ a.u. and $b = 1.28 > 1$ that contradicts to the experiment, since at ambient conditions alane is a good dielectric with finite permittivity, which equals to 4.43 (van Setten *et al.* 2007).

The reason is that according to the Pauling conception of the electronega-tivity (electronegativities of Al and H are equal to 1.61 and 2.20, correspondingly), outer Al electrons in the molecule AlH_3 are transferred to the H atoms (Pickard and Needs 2007). Therefore, the permittivity is determined by the polarizability of the ions Al^{3+} and H^-

$$\alpha_{AlH_3} = \alpha_{Al^{3+}} + 3\alpha_{H^-}$$

Electron density in crystal alane

Al

H

C. J. Pickard and R. J. Needs. *Metallization of aluminum hydride at high pressures: A first-principles study*. Phys. Rev. B 76 (2007) 144114.

Polarizability of condensed alane

$$\alpha_{\text{AlH}_3} = \alpha_{\text{Al}^{3+}} + 3\alpha_{\text{H}^-}$$

Ionization potential of the ion Al^{3+} is high (120 eV). Therefore its polarizability is small and can be neglected. Polarizability of ion H^- in vacuum is equal to 206 a.u. This gives

$$\alpha_{\text{AlH}_3} \cong 3\alpha_{\text{H}^-} = 618 \text{ a.u.}$$

This results in even higher value of the refractivity b = 11.4 > 1. Thus an estimation of the polarizability by this formulae also contradicts to the experiment.

To estimate the polarizability in condense phase it is necessary to take into consideration the fact that the Bohr radius of the outer electron of the ion H^- in the vacuum r_i = 5.8 a_0, exceeds significantly the distance between hydrogen atoms in the crystal, as well as the size of the elementary crystal cell. The exchange interaction between electrons of the neighboring ions H^- results in significant decrease of the region occupied by each electron and, as a consequence, in decrease in the ion polarizability.
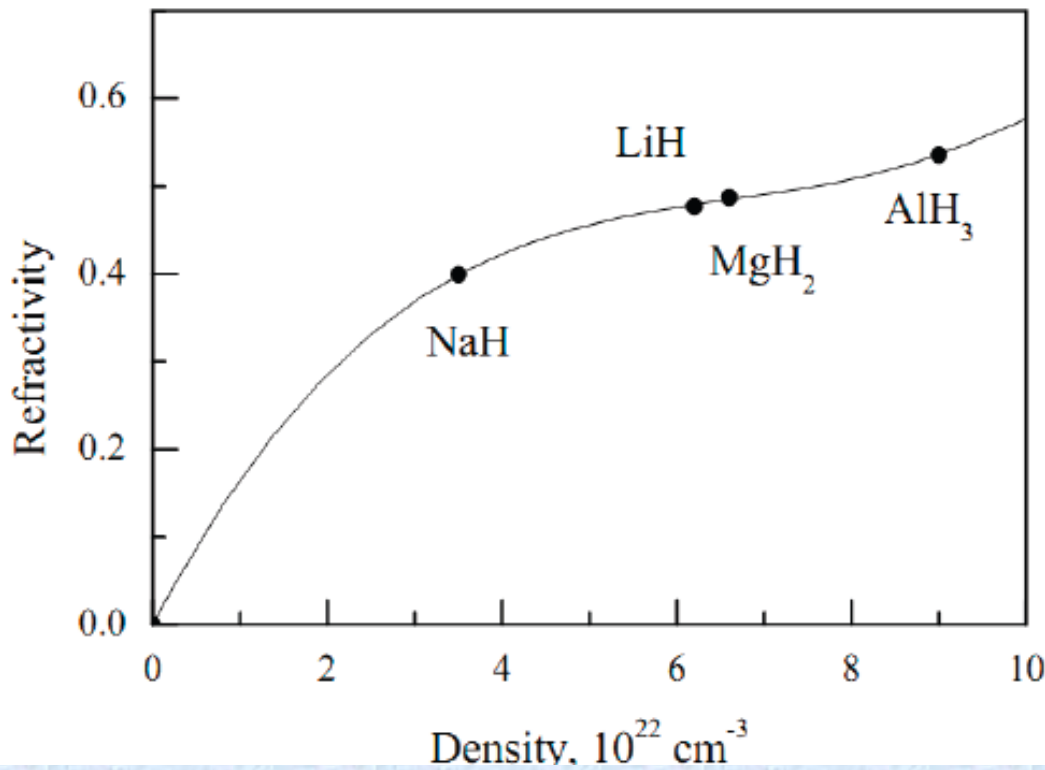
Polarizability of condensed metal hydrides

For estimation of the hydrogen negative ion polarizability we use semiempirical method previously used for the polarizability of oxides and fluorides (Shannon 1993). As a basis we take values of the permittivity ε of a number of metal hydrides calculated by Setten et al. (2007).

	ε	ρ, g·cm^{-3}	M	n, cm^{-3}	n, a.u.	b	α, a.u.
LiH	4.28	0.82	7.94	$6.2 \cdot 10^{22}$	$9.2 \cdot 10^{-3}$	0.50	12.4
NaH	3.03	1.40	24.0	$3.5 \cdot 10^{22}$	$5.2 \cdot 10^{-3}$	0.40	18.4
MgH$_2$	3.90	1.45	26.3	$3.3 \cdot 10^{22}$	$4.9 \cdot 10^{-3}$	0.49	11.9
AlH$_3$	4.43	1.49	30.0	$3.0 \cdot 10^{22}$	$4.4 \cdot 10^{-3}$	0.53	9.6
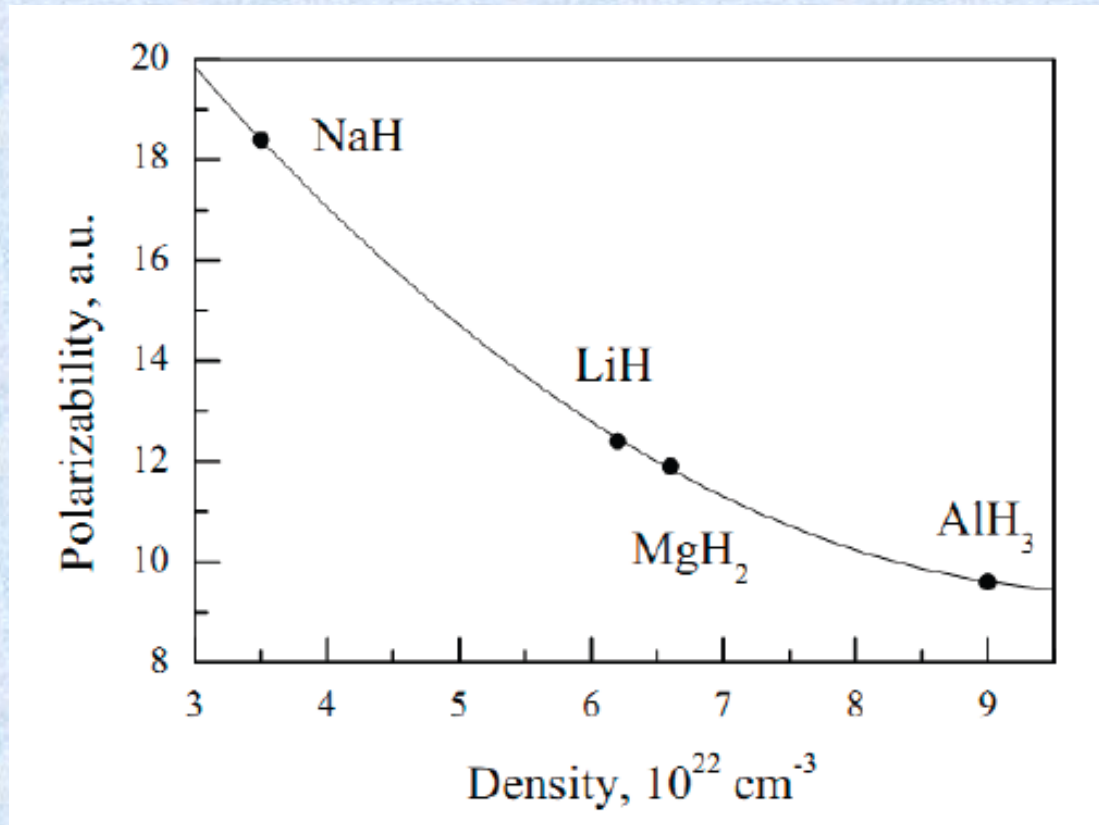
Polarizability of atomic hydrogen negative ion in condensed metal hydrides at normal conditions as a function of atomic hydrogen density.

Refractivity of condensed metal hydrides at normal conditions as a function of atomic hydrogen density.

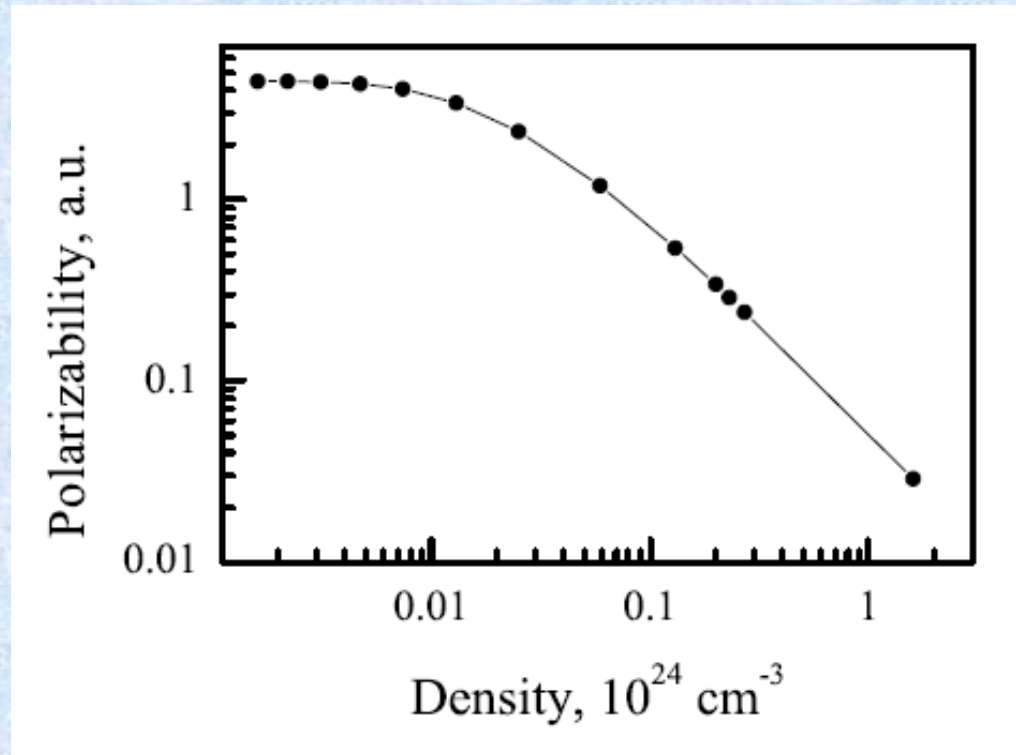$$b(n) = \frac{4\pi}{3} n\alpha(n) \cong 197.2n^3 + 265.6n^2 + 128.8n$$

$$b(n_c) = 1 \rightarrow n_c = 1.3 \cdot 10^{23} \ \text{cm}^{-3}$$

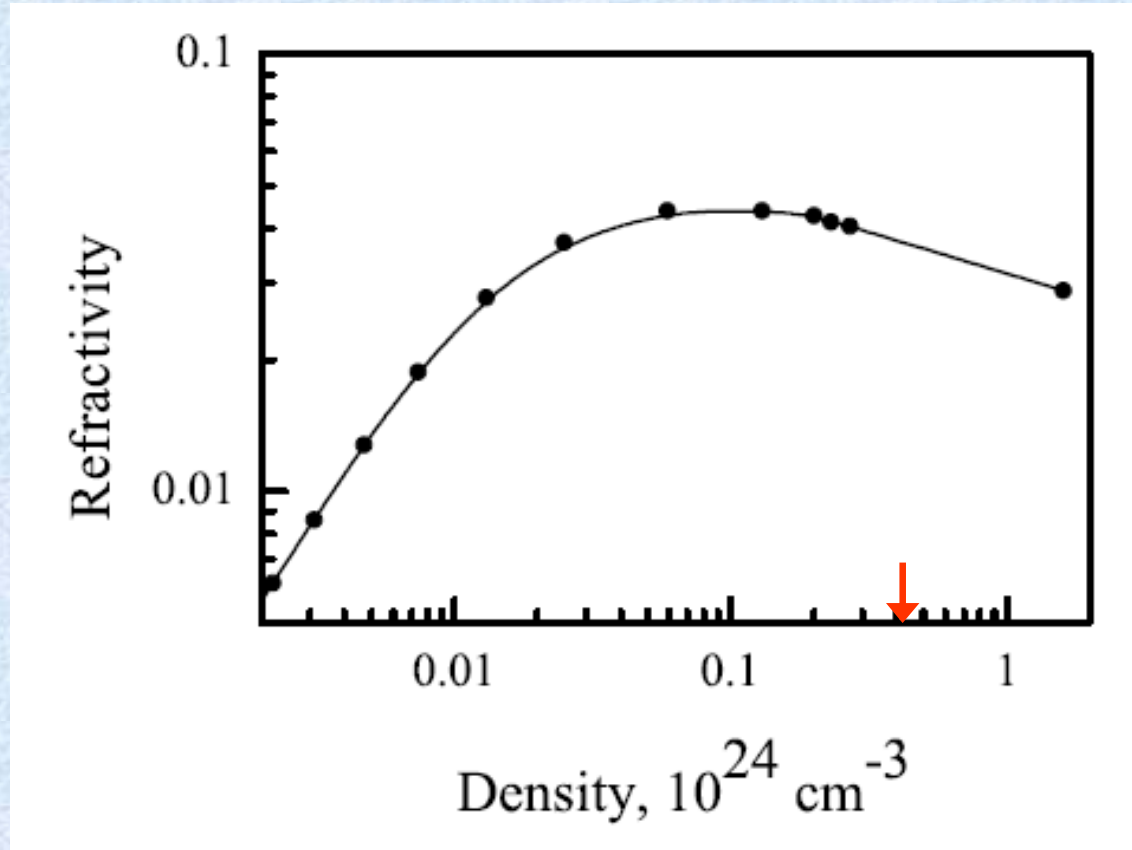$$n_c^{\exp}(\text{AlH}_3) = 1.7 \cdot 10^{23} \ \text{cm}^{-3}$$

Hydrogen

$$\alpha_H = 9/2 \text{ a.u.} \rightarrow n_m = 3.6 \cdot 10^{23} \text{ cm}^{-3} \qquad n_m^{exp} \cong 4.2 \cdot 10^{23} \text{ cm}^{-3}$$

Polarizability of atomic hydrogen as a function of atomic hydrogen density (Lauglin 2003).
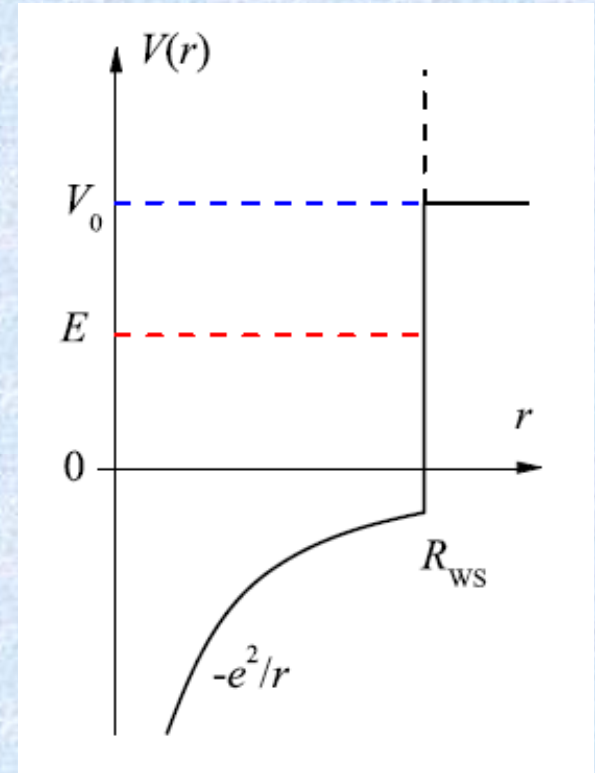
Hydrogen

Refractivity of dense hydrogen as a function of atomic hydrogen density.

Hydrogen


The ground state energy E of the hydrogen atom confined in the spherical Wigner-Seitz cell decreases with radius. At $R_{WS} < 5\,a_0$ the dependence $E(R_{WS})$ with a good accuracy is given by (Aquino 2009)

$$E \cong \frac{\pi^2}{2R_{WS}^2} - \frac{2.44}{R_{WS}} - \frac{1.08}{\pi^2} - \frac{1.21R_{WS}}{\pi^4} - \frac{1.19R_{WS}^2}{\pi^6} - \frac{0.75R_{WS}^3}{\pi^8}$$

Hydrogen

The energy of the bottom of the electron conduction band can be estimated in frame of the optical model, $V_0 \approx 2\pi Ln$. At high densities the hydrogen polarizability is small and the scattering length L is determined by the atomic core scattering, $L \approx a_0$. This gives $V_0 \approx 2\pi a_0 n_m \approx 0.39$ a.u. $= 10.7$ eV.
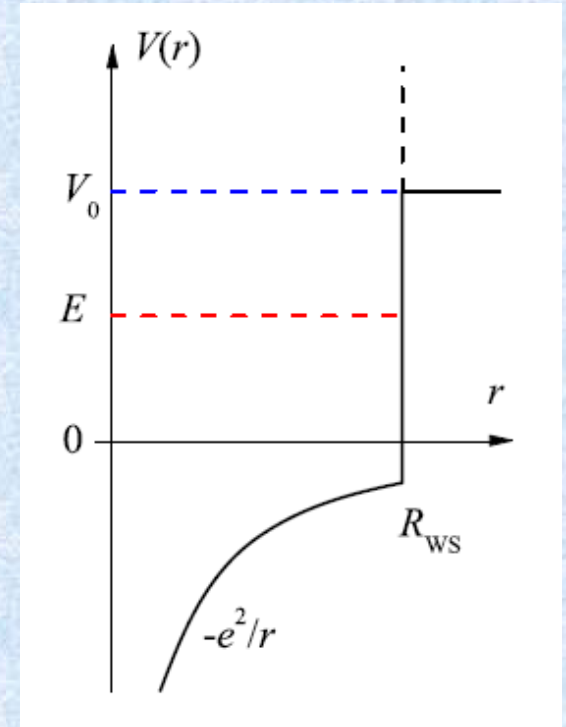
An estimation of the density of the dielectric-conductor transition n_m can be obtain from the condition $E(n_m) = V_0(n_m)$ which takes place at $n_m = 4.9 \cdot 10^{23}$ cm^{-3}. This value approaches the experimental $n_m = 4.2 \cdot 10^{23}$ cm^{-3}.

Rare gases

The conductivity of strongly compressed rare gases, such as He, Ar, Kr and Xe, rises sharply (by 3-5 orders of value) amounting values ~ 10^2-10^3 $\Omega^{-1}cm^{-1}$}, typical for liquid alkali metals (Fortov *et al.* 2003). As in the case of hydrogen, the measurements have demonstrated pronounced threshold effect. An estimation of the dielectric-conductor transition density n_m with help of the Goldhammer-Herzfeld criterion with $\alpha = \alpha_{vac}$ gives values several times (7.5 times in He) higher experimental ones.

As in the case of hydrogen the reason is in the minor role of the polarization interaction and important role of quantum size effects resulted in a shift of the electron ground state energy of confined atoms. An estimation of this effect can be obtained by accounting for the fact that at very small cell radius($\sim a_0$) ground state energy of the outer electron of an atom is practically independent on the Coulomb interaction with the core. Thus, for estimation of the Wigner-Seitz radius at which the first electron bound state appears in the cell, we can use the square well model of a finite depth. This gives for He

$$\frac{\pi^2}{8R_{\mathrm{WS}}^2(n_m)} \cong V_0(n_m) \cong 2\pi L n_m \cong 2\pi a_0 n_m \quad \rightarrow \quad n_m = 2.9 \cdot 10^{23} \ \mathrm{cm}^{-3},$$

in good agreement with the experimental value $n_m \approx 1.6 \cdot 10^{23}$ cm^{-3}.

Alkali metal dielectrization

Shock-compression investigations of Li demonstrated an abnormal behavior of the electric resistivity (Fortov *et al.* 1999, Bastea 2002). In narrow pressure region of 70-80 GPa resistivity showed drastic increase by four orders of magnitude. When pressures exceeded 80 GPa, the metallic reflection of Li showed a strong reduction. At the same time experimental observations of static-pressure-induced transformation of Na into optically transparent phase at pressure of about 200 GPa were reported (Ma et al. 2010). All these facts indicate that light alkali metals at high pressures have become insulators, or at least semiconductors.
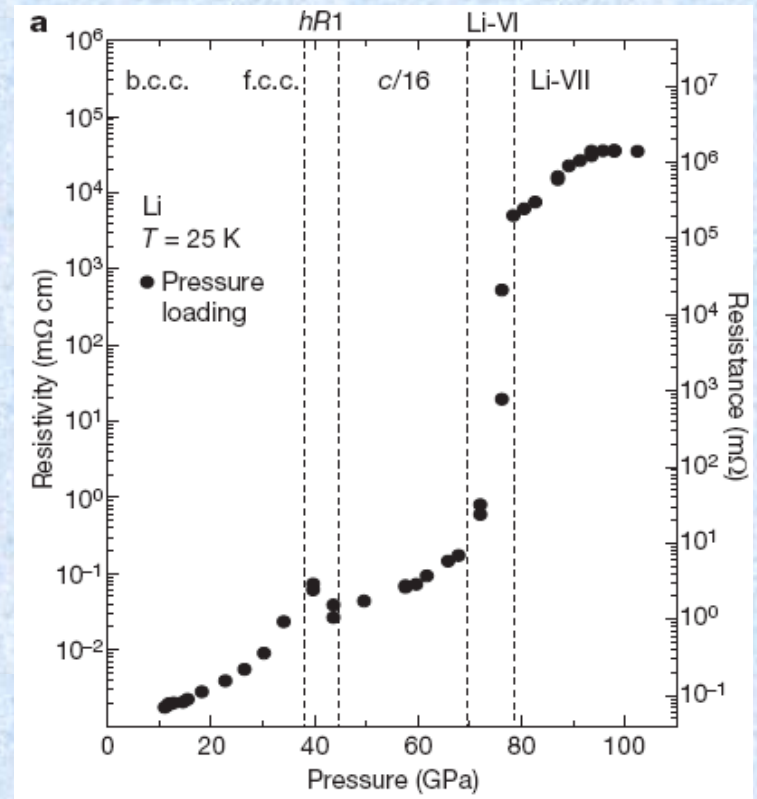
Electrical resistivity changes with pressure (Matsuoka and Shimizu 2010).

Alkali metal dielectrization

The nature of the light alkali metals dielectrization was qualitatively explained by Ashcroft (2008, 2009). It was noted that the combined effects of Coulomb repulsion, Pauli exclusion, and orbital orthogonality push electrons away from the ionic cores and form piles of charge at interstitial regions. These piles of electronic charge are rather isolated one from another. At high pressures and densities lithium and sodium became very similar to "electride", where the localized interstitial electrons play the role of the anions. However, it is interesting to look for a qualitative explanation of the phenomenon in frames of the conception of "dielectric catastrophe". More exactly it should be called as "inverse dielectric catastrophe", as far as initially Li and Na are conductors and then under strong compression they become dielectrics.

Alkali metal dielectrization

To use Herzfeld-Goldhammer criterion for estimation of the metal-dielectric transition density of alkali metals we have to know the polarizability of the positive ions and localized electrons. The polarizabilities of Li^+ and Na^+ are equal to 0.192 and 1.00 a_0^3, correspondingly. They can only decrease with density. For rough estimation of the localized electron polarizability we use the model of electron confined in impenetrable 3D spherical potential: $U(r) = 0$, $r \leq R$; $U(r) = +\infty$, $r > R$. The polarizability was calculated by conventional perturbation theory. As result we have

$$\alpha_e = \frac{64\pi^6}{\sqrt{3}} \frac{R^4}{a_0} \sum_{n>0} \frac{1}{c_n^2(c_n^2 - \pi^2)^5}, \quad \tan c_n = c_{n,} \quad R < R_{WS}$$

The main contribution is given by the first term of the sum with $a_1 = 4.49$. This gives $\alpha_e \approx 0.015R^4$. The metal-dielectric transition of light alkali metals takes place at (4-5)-fold compression or at $R_{WS} > 2a_0$. It means that the total refractivity $b = b_i + b_e < \alpha_i/(R_{WS})^3 + 0.015R_{WS} \ll 1$. Hence, the polarization interaction does not play significant role in the region of the metal-dielectric transition of light alkali metals.

Alkali metal dielectrization

The metal-dielectric transition is connected with pure quantum effect of the electron localization in the interstitial regions. Subsequent enhance of the compression decreases the size of the interstitial regions and increases the kinetic energy of localized electrons due to the quantum size effect. This can give rise to disappearance of the bound levels inside interstitial regions and in the electron transition into the conducting band. This mechanism can be responsible for decreasing of the lithium mobility with density observed in multiple shock-wave experiment at pressures about 200 GPa (Fortov *et al.* 2002) and in the diamond anvil cells at pressures about 100 GPa (Matsuoka and Shimizu 2010).

Conclusion

In the present work we considered how phenomenological conception of the "dielectric catastrophe" can be applied to the dielectric-conductor transition, observed in various substances. We have shown that this conception can be useful in case of metal hydrides, provided the correct description of polarizability dependence on the density, $\alpha(n)$. Besides, it is necessary to account for the enhanced polarization interaction. Then, in particular, the cell model can be applied to obtain $\alpha(n)$. For the case of hydrogen, rare gases and alkali metals this conception does not give rise to the correct transition density as far as the polarization interaction is of minor importance for given substances under conditions in hand. But the cell model, namely, the electron confined in impenetrable spherical potential, are still applicable. For farther investigations it is necessary to use more refined theories, which can be the aims of future work.