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A Relation between the Gap Energy and the Dielectric Constant in Semiconductors of Diamond Structure

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(30.VI.63)

Zusammenfassung. Es wird gezeigt, dass die Clausius-Mossotti-Formel zusammen mit Kirkwoods Gleichung für die Abhängigkeit der Atompolarisierbarkeit vom Atomradius r eine Funktion $\epsilon(r)$ für halbleitende Elemente der IV. Gruppe liefert.

Weiterhin wird eine Beziehung $\Delta E(r)$ postuliert und eine Gleichung für diesen Zusammenhang vorgeschlagen. Auf diese Weise ist es möglich eine $\epsilon(\Delta E)$ Beziehung herzuleiten.

Die auf rein empirischem Weg abgeleitete Moss-Relation

$$\epsilon^{-2} = \text{Konst.} \cdot \Delta E$$

ist eine ebenfalls mögliche Beschreibung von $\epsilon(\Delta E)$.

Zwischen der hier hergeleiteten $\epsilon(\Delta E)$ -Abhängigkeit und der Moss-Relation kann auf Grund der verfügbaren experimentellen Daten nicht definitiv entschieden werden.

Mit unseren Überlegungen lässt sich die Gültigkeit der $\epsilon(\Delta E)$ Beziehung auch für halbleitende Verbindungen verstehen.

Summary. The object of this paper is to show that using the Clausius-Mossotti formula together with Kirkwoods equation for the relation between the atomic polarizability and the atomic radius r yields an expression $\epsilon(r)$ for the static dielectric constant of group IV semiconducting elements.

Further, a relationship $\Delta E(r)$ has been postulated and a formula for this correlation has been suggested.

With these two relations it is possible to derive an expression $\epsilon(\Delta E)$.

The Moss relation $\epsilon^{-2} = \text{const.} \cdot \Delta E$ which has been found on a purely empirical basis also represents a description of $\epsilon(\Delta E)$.

With the experimental data available it is not yet possible to decide clearly whether the Moss relation or our expression is more accurate.

The considerations represented in this paper should apply also to semiconducting compounds.

1. Introduction

As has been pointed out first by Moss¹⁾²⁾ and later by WELKER³⁾ (p. 328), ARMSTRONG⁴⁾ and others, a relation exists for semiconductors of the form

$$\epsilon^{-2} = \text{const.} \cdot \Delta E \quad (1)$$

called the Moss-relation which is surprisingly well fulfilled for elements as well as for numerous semiconducting compounds. ϵ means the relative static dielectric constant and ΔE the width of the energy gap. This relation is not only of basic interest but can also be very useful as a rule for the prediction of properties of new semiconducting inorganic compounds.

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Recently COLE⁵⁾ has taken up again the idea of MOSS¹⁾ in order to explain the relationship (1). He used the well-established hydrogen-model for shallow impurities which actually leads to a connection between ε^{-2} and the ionization energy of the impurity. However, it seems to be very doubtful whether this model can be applied in general to yield a relation between ε^{-2} and the energy gap in semiconducting crystals.

Therefore we take up the problem again and try to find an answer to the following questions:

1. is there any theoretical reason for a relation $\varepsilon = \varepsilon(\Delta E)$ to exist?
2. can this relation be of the special form (1)?
3. if 1. and 2. turn out not to be fulfilled is there any more general relation from which under special circumstances (1) may be derived?

It seems to be obvious that in order to answer these questions one should start with a connection between ε as a macroscopic property of crystals and the polarizability as a property of their atoms. So one arrives at the Clausius-Mossotti formula.

We restrict ourselves to the properties of group IV semiconducting elements. Semiconducting compounds will be discussed at the end of this paper.

2. ε of the Lattice and Polarizabilities of the Group IV Elements

The four elements C, Si, Ge and Sn (specificly the modifications diamond and α -Sn) crystallize in the diamond lattice, one of the diagonal cubic lattices described by BORN and GÖPPERT-MAYER⁶⁾. If an electrostatic field is applied to a crystal of this type the influence of its neighbours on a single atom can be calculated according to LORENTZ⁷⁾. The static dielectric constant of the lattice is then given by the Clausius-Mossotti*) formula

$$\frac{\varepsilon-1}{\varepsilon+2} = \frac{4\pi}{3} \cdot N \cdot \frac{\varrho}{M} \cdot \alpha, \quad (2)$$

N = Loschmidt number, ϱ = density of the material, M = molecular weight. Here we understand the interpretation of the "macroscopic" Clausius-Mossotti formula (2) as a "molecular" expression in the same sense as given by FRÖHLICH⁷⁾ (p. 170ff). Then α represents the polarizability of the atom in its lattice-site. The right side of (2) may be expressed by α/κ where the factor $M/\varrho N$ in $\kappa = 3M/4\pi\varrho N$ means the volume V_0 available to a single atom. This reinterpretation of (2) requires the additivity of the atomic polarizabilities to give the molar polarizability⁷⁾ (p. 171).

Recently WISER⁸⁾, using a self-consistent field method, derived equation (2) for the dielectric constant in the tight binding limit. He has shown that α is just the atomic polarizability of an isolated atom in an applied field.

Our further interest will be now concentrated on the properties of the atomic polarizability α . KIRKWOOD⁹⁾ derived for the atomic polarizability α an expression containing the number of electrons and a meanvalue of the quadrupolemoment of the electron distribution, compare also BUCKINGHAM¹⁰⁾, formula II A:

$$\alpha = \frac{4}{9} a_0^3 \sum_{nl} 2(2l+1) \langle r^2 \rangle_{nl, nl}^2.$$

*) This seems to be the right way of writing the name according to MOSSOTTI himself in *Annali della Università Toscane* Vol. I, p. 181 (1846).

According to BUCKINGHAM $(r^2)_{nl, nl}$ has to be interpreted as an average value of r^2 (in atomic units) with respect to the charge density. l means the azimuthal quantum number.

Since the radii of the different orbits enter the expression for α , only electrons in the outermost orbit give a significant contribution.

For a spherical charge distribution one gets therefore $\alpha \sim r^4$, where r is the atomic radius, used in the sense of SLATER¹¹⁾ throughout this paper.

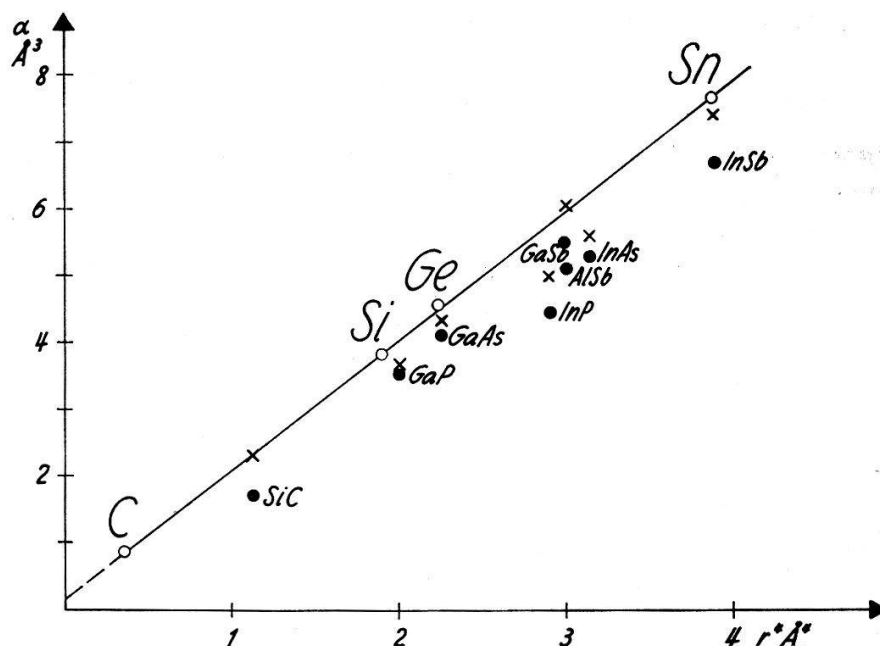


Figure 1

α calculated using (2) and plotted according to KIRKWOOD⁹⁾.

○ elements, ● compounds, where $1/2 (r_i^4 + r_k^4)$ is used instead of r , × calculated with formula (9), and with the slope K of the straight line for the elements

Figure 1 shows that this relation is surprisingly well fulfilled for the afore mentioned elements. The absolute values however do not agree with the theory. This might be due to the fact that only the electrons in the outermost shell are considered to contribute to the polarizability**) and that calculated values of atomic polarizabilities show good agreement with measured values only in exceptional cases, compare table 5 given by DALGARNO¹²⁾. So we take in equation (3)

$$\alpha = K \cdot r^4 + b, \quad (3)$$

the constants K and b evaluated from Figure 1 to adjust the theoretical relation to the experimentally determined values which have been calculated from the experimentally determined ϵ using equation (2).

3. The Relation $\Delta E(r)$

Since the gap energy ΔE is a function of the symmetry properties of the lattice and the electronic state of the atoms building up the lattice as well, a functional dependence of ΔE on the atomic radius r for each structure is to be expected.

**) It should be mentioned however, that b is about a hundred times the polarizability of C^{4+} .

From known energy band structure calculations in diamond type lattices the following conclusions can be drawn (compare^{13), 14), 15) and the literature given in these papers):}

a) The energies E of electronic states in a crystal are in general given by functions $E(k, a)$ of the reduced wave vector k and the lattice constant $a = 8r/\sqrt{3}$. With a certain absolute accuracy only calculations for $E(k) = E(k, a)/a = \text{const.}$ have been published (compare for instance¹³⁾¹⁶⁾ using the experimentally determined value for the lattice constant a . $E(a) = E(k, a)/k = \text{const.}$ calculations lead in general to a theoretical determination of a ¹⁷⁾. Available results are considerable less accurate than $E(k)$ calculations (compare the discussion in¹³⁾) and the use of experimentally determined values of the lattice constant is generally preferred.

b) If the lattices of diamond, Si, Ge and α -Sn were exact homologous, a $\Delta E(a)$ -function at constant values k would be obtainable.

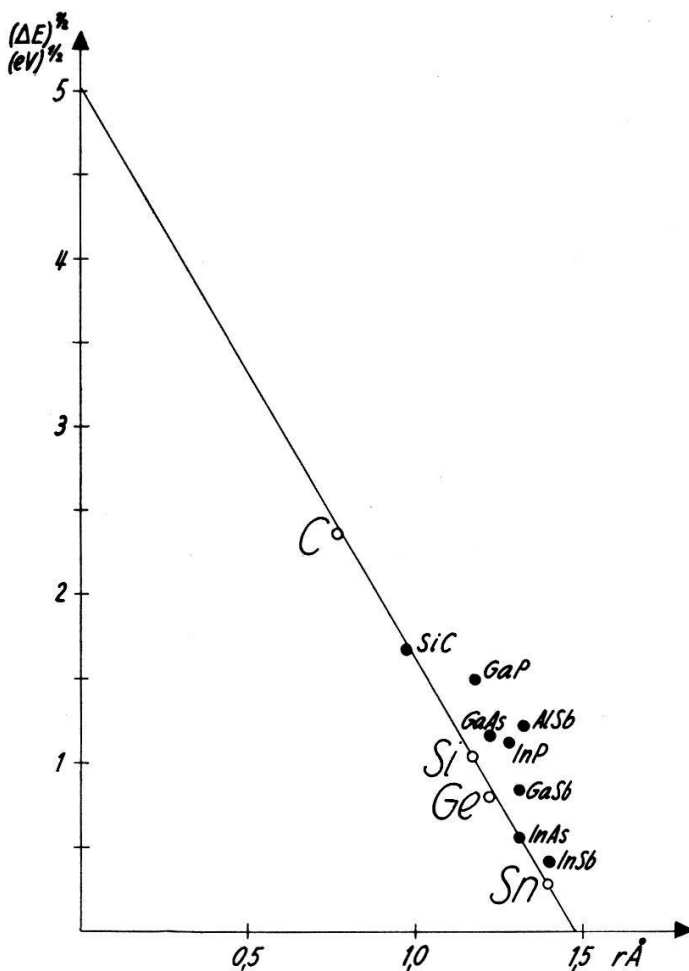


Figure 2

$(\Delta E)^{1/2}$ as a function of the atomic radius.

○ elements, ● compounds, where

$\frac{1}{2}(r_i^4 + r_k^4)$ is used instead of r

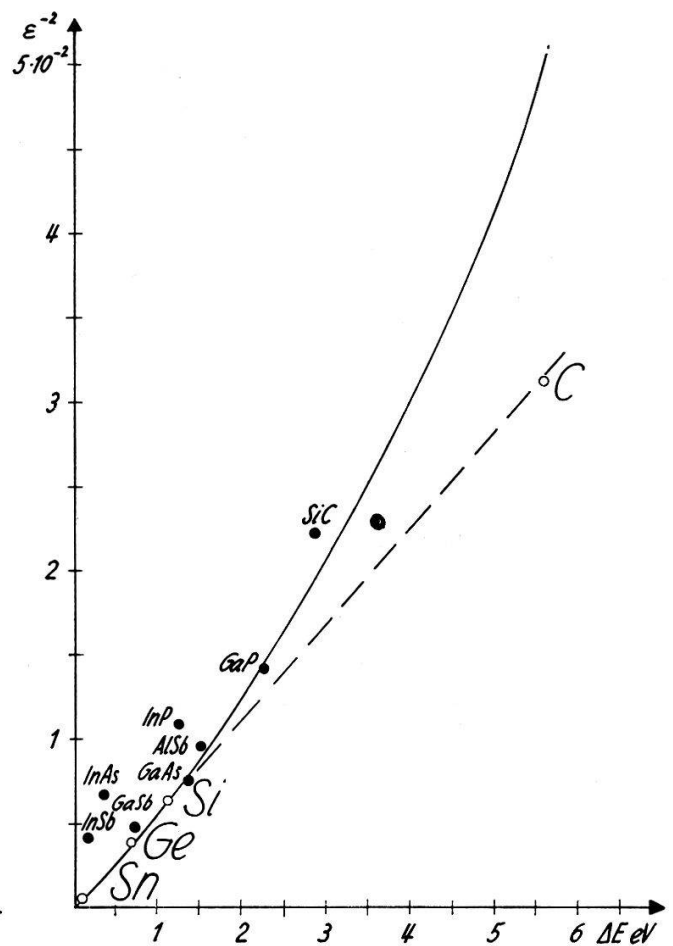


Figure 3

ϵ^{-2} as a function of ΔE .

(---) Moss-relation, (—) represents formula (8), ○ elements, ● compounds

c) However, the energy bands of the group IV elements show an increasing sensitivity to small variations of the crystal potential with increasing atomic number¹⁸⁾¹⁹⁾ (p. 1224). Furthermore the valence electron wave functions are different because of different main quantum numbers²⁰⁾. In addition it must be mentioned that

spin-orbit-coupling effects increase with increasing atomic number¹³⁾ (p. 114),²¹⁾ (p. 1165) and ¹⁵⁾ (p. 246). Therefore we expect small but significant differences in the $E(k)$ -structure of the four elements, comp. ¹⁴⁾, ²⁰⁾ and ¹⁶⁾. If $E(k, a)/k = \text{const.}$ is plotted against a , these differences will lead in general to discontinuities in the functional dependence, as must be concluded from ¹⁴⁾.

d) In conclusion we expect that because of the differences in the $E(k, a)/a = \text{const.}$ structure for the elements no continuous function $\Delta E(a)$ exists. If any values $\Delta E(a)$ can be calculated with sufficient accuracy only the four values corresponding to the elements are significant, the accuracy obtainable by so far is not sufficient for our purpose.

The only possibility which leads to results of sufficient accuracy is to set up an empirical relation. In this way we also take into consideration only the four values ΔE for the elements. Several empirical relations for $\Delta E(a)$ have been suggested in the literature, GOODMAN²²⁾, SUCHET²³⁾, MIYAUCHI²⁴⁾, CZAJA²⁵⁾ and LANDER²⁶⁾. However none of these relations is useful for our purpose, since either they do not include ΔE for diamond (²²⁾, ²³⁾, ²⁴⁾) or they show rather large deviations from the observed behaviour (²⁵⁾, ²⁶⁾). We found that the relation

$$(\Delta E)^{1/2} = -A \cdot r + B \quad (4)$$

fits the experimental data for all four elements better than the relations mentioned before, as long as the lower limit for ΔE of diamond ($= 5,6 \text{ eV}^{27)$) is taken, comp. figure 2.

Empirical relations as mentioned above lead to a critical radius $r_{\text{crit.}}$ for $\Delta E = 0$.

According to (4) and figure 2 we get

$$r_{\text{crit}} = \frac{B}{A} = 1,47 \text{ \AA}$$

r_{crit} is to be interpreted as the upper limit of the atomic radius up to which non-metallic behaviour can be expected in the structure considered. This interpretation is supported by MOTT²⁸⁾ who considered the transition to metallic conduction in semiconductors. It is interesting to remark that r_{crit} also seems to lead to an upper limit for the lattice constant of diamond (and zink-blend) structure ($a \leq 6,8 \text{ \AA}$), which is in accordance with the observed values for elements and binary compounds.

4. The Dependence of E on ΔE

The volume available to a single atom with radius r in the lattice is

$$V_0 = \frac{4\pi}{3} r^3 \gamma. \quad (5)$$

Since eight times V_0 is the total volume of the unit cell in the diamond structure (lattice constant $a = 8r/\sqrt{3}$), the relative volume γ^{-1} occupied by an atom is $\gamma^{-1} = \sqrt{3}\pi/16$ and (see section 2)

$$\kappa = \gamma \cdot r^3. \quad (6)$$

From equations (3) and (6) we get

$$\frac{\alpha}{\kappa} = \frac{K}{\gamma} \cdot r + \frac{b}{\gamma \cdot r^3}. \quad (7a)$$

In the "limiting case of metallic conductivity" where $\Delta E = 0$ and $\varepsilon \rightarrow \infty$, we have

$\alpha/\kappa \rightarrow 1$, and consequently the constants K, b, γ, A, B are related to each other in the following way:

$$\frac{K}{\gamma} \cdot \frac{B}{A} + \frac{b}{\gamma} \left(\frac{A}{B} \right)^3 = 1.$$

Numerical values of the constants evaluated from the graphs in figures 1 and 2 fulfill this relation within the limits of 50%. Representative values of the constants are $K = 1.96 \text{ \AA}^{-1}$, $b = 0.15 \text{ \AA}^3$, $A = 3.43 \text{ eV}^{1/2} \text{ \AA}^{-1}$, $B = 5.03 \text{ eV}^{1/2}$, $\gamma = 2.94$.

(7a) yields with (4) and (2) the following expression

$$\frac{1}{\varepsilon^2} = \frac{F^2 \cdot \Delta E}{(3 - 2 F (\Delta E)^{1/2})^2}. \quad (8)$$

From $F = K/\gamma A$ and with the numerical values for K, γ and A , F is computed to be $F = 0.194 \text{ eV}^{-1/2}$. This value when substituted into Equation (8) yields ε^{-2} for the semiconducting elements of group IV. In figure 3 the results are compared with the experimental data.

As can be seen, the only value leading to a difference between Moss' postulated linear relation and (8) is that of diamond. ΔE for diamond is calculated from the absorption limit²⁷⁾²⁹⁾. It is well known, however, that determining ΔE from optical data involves a lot of interpretation, compare GEBALLE in²⁶⁾ (p. 333),²⁷⁾ and no such attempt is known for diamond. ΔE for diamond is therefore by far not determined to the same accuracy than ΔE for Si and Ge. For this reason it is not yet fully established whether (8) or the Moss relation represents the experimental behaviour.

5. Discussion

The advantage of deriving a function $\varepsilon(\Delta E)$ by using an empirical relation $\Delta E(r)$ instead of postulating directly an empirical function $\varepsilon(\Delta E)$ is the following:

There are several reasons for a function $\Delta E(r)$ to exist, which is unknown at the moment, which is probably very complicated and if calculated with the known procedures probably too inaccurate to be significant.

With this in mind, we see that setting up an empirical relation $\Delta E(r)$ by means of which formula (9) can be derived gives a certain amount of information about the origin of a function $\varepsilon(\Delta E)$.

We are now in a position to discuss the extension of (8) to binary semiconducting compounds.

In general compounds have a larger ΔE than that calculated from (4) with the meanvalue of the radii. This is to be expected since, due to the partial ionic character the binding energy in compounds is higher (comp. ^{30), 31)}). If the polarizability for a compound was the same as that for an element with the corresponding meanvalue for r , this compound would be represented according to (8) by a point beneath the curve in figure 3. However, the polarizabilities of compounds are generally smaller than those for corresponding elements*) and the point representing the compound in

*) This is to be expected. Equation (3) and the additivity rule for the polarizabilities, comp. ROBERTS³²⁾, yields for $i-k$ compounds:

$$\alpha_{ik} = \frac{K}{4} \left(\frac{i \cdot r_i^4 + k \cdot r_k^4}{2} + b \right) \quad (9)$$

which is smaller than α_{IV} , if the radii are different. As shown in figure 1 this is more or less fulfilled. Deviations from (9) may be due to the partly ionic character of these compounds, according to FOLBERTH³³⁾.

figure 3 is shifted upwards. Because of this compensation a large number of compounds happen to follow nearly the same $\varepsilon(\Delta E)$ dependence as the elements. This aforementioned compensation, however, is not exactly fulfilled and one expects the compound values being more scattered around the $\varepsilon(\Delta E)$ -function than the values for elements. This has actually been found¹⁾²⁾. Furthermore we are able to explain in this way – at least qualitatively – the exceptionally large deviations of InSb and InAs (compare ²⁾).

As a result of our paper we want to stress our statements for the semiconducting group IV elements:

a) From the Clausius-Mossotti formula (2) connecting the dielectric constant ε of a crystal with the polarizability α of its atoms and Kirkwood's equation giving the dependence of the atomic polarizability α on the atomic radius r , an equation $\varepsilon(r)$ can be derived without further assumptions for the semiconducting group IV elements.

b) If in addition an empirical $\Delta E(r)$ dependence is taken into account, one arrives at a $\varepsilon(\Delta E)$ -relation which is similar to but not identical with the Moss relation derived on a purely empirical basis. Without having a better knowledge on ΔE for diamond it is not possible to decide which one of these two relations fits better the experimental points.

In contrast to the $\varepsilon(r)$ equation mentioned above the $\varepsilon(\Delta E)$ dependence is theoretically not more significant than the $\Delta E(r)$ dependence used.

c) The advantage of our derivation is besides clarifying the statements made in a) and b) that it gives the possibility to show why semiconducting binary compounds follow nearly the same (ΔE) -relation as do the group IV elements.

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Table I

| | $r^a)$ | ΔE | ε | $\alpha^b)$ |
|--------------|--------|-----------------------|--------------------|---------------------|
| C | 0.77 Å | 5.6 eV ²⁷⁾ | 5.68 ^{c)} | 0.82 Å ³ |
| Si | 1.17 | 1.12 ³⁰⁾ | 12.5 ^{d)} | 3.82 |
| Ge | 1.22 | 0.66 ³⁰⁾ | 16.0 ^{d)} | 4.54 |
| α -Sn | 1.40 | 0.08 ³⁰⁾ | 47.0 ^{e)} | 7.68 |
| GaAs | 1.22 | 1.35 ³⁰⁾ | 11.5 ²⁾ | 4.10 |
| GaP | 1.18 | 2.24 ³⁰⁾ | 8.4 ²⁾ | 3.46 |
| GaSb | 1.31 | 0.71 ³⁰⁾ | 14.5 ²⁾ | 5.51 |
| InAs | 1.31 | 0.35 ³⁰⁾ | 12.2 ²⁾ | 5.28 |
| InP | 1.28 | 1.25 ³⁰⁾ | 9.6 ²⁾ | 4.45 |
| InSb | 1.40 | 0.16 ³⁰⁾ | 15.7 ²⁾ | 6.7 |
| AlSb | 1.32 | 1.52 ³⁰⁾ | 10.2 ²⁾ | 5.1 |
| SiC | 0.97 | 2.86 ³⁰⁾ | 6.7 ²⁾ | 1.67 |

a) Covalent (atomic) radii according to PAULING³⁴⁾, for compounds r is replaced by $1/2 (r_i + r_k)$.

b) Calculated with formula (2).

c) See ⁷⁾ p. 109.

d) See ³⁵⁾ Vol. Si part B, p. 110.

e) Calculated value according to Moss¹⁾ with $\Delta E = 0.08$ eV³⁶⁾. This value has been confirmed

indirectly through the coincidence of measured and calculated activation-energies of donors in α -Sn. The calculated polarizability is rather insensitive on uncertainties in ϵ since here $\epsilon \gg 1$. A similar value for ϵ has been given by ARMSTRONG⁴).

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