

the Thomas-Fermi model<sup>1</sup> (denoted by  $\kappa_1$ ) and the electronic theory of metals<sup>2</sup> (denoted by  $\kappa_2$ ). The values of  $R_1$  and  $R_2$  used in the calculation were taken from Zhdanov<sup>7</sup>, and the experimental values of  $\kappa$  were obtained from Ref. 8. It was assumed that  $z = 2$  in the case of all the metals except for the alkali metals which have  $z = 1$ . The calculation could not be made for many metals (W, Zr, Mo, Ta, Nb, Bi, Sb, etc.) because of the lack of data on the ionic radius with the given number ( $z = 2$ ) of valence electrons.

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## SUMMARY

Using the concept of the volume of valence electrons, a formula has been derived for the compressibility of metals which is applicable to metals of various Groups of the Periodic System. The predicted variation of the compressibility with the atomic radius is similar to that obtainable from the Thomas-Fermi model.

1. N. Gombash, "Statistical Theory of the Atom and Its Application" (Translated into Russian), Inostr. Lit., 1951, p. 317.
2. A. S. Kompanets, "Teoreticheskaya Fizika" (Theoretical Physics), GTTI, 1957, p. 455.
3. G. G. Gel'man, "Kvantovaya Khimiya" (Quantum Chemistry), ONTI, 1937, p. 24.
4. W. Biltz, Z. anorg. Chem., **223**, 321 (1935).
5. V. V. Tarasov and B. P. Bering, Zhur. Fiz. Khim., **13**, 214 (1939).
6. L. D. Landau and E. M. Lifshits, "Elektrodinamika Sploshnykh Sred" (Electrodynamics of Continuous Media), Fizmatgiz, 1959, p. 48.
7. G. S. Zhdanov, "Fizika Tverdogo Tela" (Solid State Physics), Izd. Moskov. Gos. Univ., 1961, p. 184; "Kratkii Spravochnik Fiziko-Khimicheskikh Velichin" (Short Handbook of Physico-chemical Quantities), Goskhimizdat, 1959; L. Pauling, "The Nature of the Chemical Bond" (Translated into Russian), Goskhimizdat, 1947, pp. 180, 337, 396.
8. "Spravochnik Metallurga po Tsvetnym Metallam" (The Non-Ferrous Metallurgist's Handbook), Vol. 1, Metallurgizdat, 1953.
9. A. F. Kapustinski, Zhur. Struktur. Khim., **1**, 216 (1960).

Mendeleev Institute of  
Chemical Technology,  
Moscow

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## EFFECT OF ATOMIC COORDINATION ON THE TEMPERATURE VARIATION OF HEAT CAPACITY AT LOW TEMPERATURES

V. A. Romanovskii

It is known that the temperature variation of the heat capacity of various substances does not obey a single law. The form of the heat capacity curve of any substance depends on the properties of the chemical bond, the ratio

of the masses of different atoms, and the crystal-chemical structure of the substance. The effect of structural peculiarities of such groups of substances as molecular, chain, and layer crystals on the temperature variation of heat capacity has been examined by Born<sup>1</sup> and Tarasov<sup>2,3</sup>, who modified the Debye theory to take into account the specific features of the structure of the above crystals. The experimental heat capacity curves for these crystals exhibit a much greater deviation from the Debye theory than those for crystals with a continuous three-dimensional framework comprising identical chemical bonds. But even among the latter, although the majority do obey satisfactorily the Debye function, there are some which exhibit a pronounced deviation from it.

The aim of the present work is to show that the extent of deviation of the heat capacity curve for a crystal from the Debye function is largely determined by the magnitude of the atomic coordination with nearest neighbours. The problem is solved by comparing experimental low-temperature heat capacities and atomic coordinations of various substances. Before making this comparison, however, it is necessary to take into account the following consideration. The applicability of the Debye model (an isotropic elastic continuum) to a real crystal with a single type of bonding depends not only on the chemical bond but also on the ratio of the atomic masses and on the atomic coordination. In this respect the closest approach to an isotropic continuum is obtainable with structures having the maximum coordination with respect to nearest neighbours, *i.e.* having the closest packing with a coordination number of 12. Any decrease in the coordination number will therefore lead to an increase in the difference between the Debye model and the properties of a real crystal.

As will soon be made evident, the above postulate is in good agreement with experimental data for the heat capacities of a large number of crystals. It should be noted that the difference between experimental heat capacities at constant pressure and those at constant volume, to which the present theory applies, becomes substantial at relatively high temperatures. Therefore, to a first approximation, in comparing experimental data with the theory we shall set an upper limit to the reduced temperature, *i.e.*  $T/\theta_D = 0.3$ . In the Table the criterion reflecting the deviation of experimental heat capacities of substances having different atomic coordinations from the Debye theory, is the ratio of the maximum and minimum characteristic Debye temperatures, denoted by  $\theta_{D_{max}}/\theta_{D_{min}}$ . The values of this ratio for the substances listed in the first and second rows of the Table have been taken from Eucken's review<sup>4</sup> or calculated from the graphs in Blackman's review<sup>5</sup>. Those for  $\text{SiO}_2$ ,  $\text{GeO}_2$ , and  $\text{B}_2\text{O}_3$  have been calculated by the author from experimental data<sup>6-8</sup>. When a substance rigorously obeys the Debye law,  $\theta_{D_{max}}/\theta_{D_{min}} = 1$ .

Substances	C.N. or M.C.N.	$\theta_{D_{max}}/\theta_{D_{min}}$
Au, Pb, Na, K, Mo, Pt, Cu, Al, Ag, Fe, KCl, FeS <sub>2</sub> , LiF, KBr, CaF <sub>2</sub>	12-5.3	not more than 1.13
Ge, Si, Sn(grey), ZnS	4	1.43-1.6
SiO <sub>2</sub> , GeO <sub>2</sub> , B <sub>2</sub> O <sub>3</sub>	2.66-2.4	~2.17