PHYSICAL REVIEW VOLUME 91, NUMBER 3 AUGUST 1, 1953

The Surface Tension of Liquid Silicon and Germanium*

PAUL H. KECK AND WENDELL VAN HORN
Signal Corps Engineering Laboratories, Fort Monmouth, New Jersey

(Received April 27, 1953)

The surface tensions of liquid silicon and germanium were determined using the drop weight method. 600 dynes/cm was found for germanium and 720 dynes/cm for silicon at their freezing points and argon atmosphere. The parachors of the group IVb elements as derived from surface tension measurements of the molten elements are compared with the atomic parachors calculated from compounds. The differences are interpreted as structural parachors which indicate that the bonding between neighboring atoms in the liquid state increases in nearly uniform steps from lead to tin and to germanium. No further increase of the structural parachor takes place in silicon which is consistent with the fact that only four electrons per atom are available for bonding.

IN connection with the problem of producing single crystals of germanium and silicon from the melt, the values of the surface tensions of these elements in the liquid state at their freezing points are of interest. Since no data could be found in the literature the surface tensions were measured via the well-known drop weight method.

A short tantalum cylinder of approximately 25 mm diameter was suspended in a quartz glass flask, and a concentric induction coil on the outside served to heat the cylinder to incandescence in argon as an inert atmosphere. Rods of high-purity polycrystalline germanium and of silicon, up to about 5 mm diameter, were slowly lowered into the incandescent cylinder whereby the tip melted and a drop of gradually increasing size was formed. The process was slowly continued until the drop fell off. Proper melting was obtained with the temperature of the tantalum cylinder adjusted to approximately 1400°C for germanium and 2000°C for silicon.

The surface tension γ was calculated from the radius r of the rod and the weight W in grams ($=gW$ in dynes) of a drop according to the equation,

$$\gamma=\phi gW/2\pi r[\text{dynes/cm}], \tag{1}$$

where ϕ is a correction factor which is dependent upon the cross section of the rod and upon the volume of the drop. Values of ϕ were calculated and measured for various substances by Lohnstein and Harkins and co-workers.[1]

The results of our measurements of the surface tensions are

$$\gamma=600 \text{ dynes/cm for germanium,}$$
$$\gamma=720 \text{ dynes/cm for silicon.}$$

These values refer to the liquids at the freezing point in argon of atmospheric pressure and are believed to be accurate at least within ±5 percent.†

Since various relations are known between the surface tension and other physical and chemical quantities, a number of conclusions can be deduced from the knowledge of the surface tension. Macleod found that the fourth root of the surface tension divided by the density is independent of temperature,

$$\gamma^{\frac{1}{4}}/(\rho_L-\rho_G)=\text{constant}, \tag{2}$$

where ρ_L and ρ_G refer to the densities of the liquid and the gas phase. ρ_G can ordinarily be neglected.

Sugden[2] introduced the parachor P which is the expression in (2) multiplied by the molecular weight M and showed that P can provide some insight into the bonding between the atoms,

$$P=\gamma^{\frac{1}{4}}M/(\rho_L-\rho_G)$$

or

$$P=\gamma^{\frac{1}{4}}V, \tag{3}$$

where V is the molar volume of the compound or the atomic volume in the case of an element. The parachor of a compound is an additive property, being the sum of the atomic parachors with some additional terms which account for binding forces between the atoms.

Table I summarizes the values for the elements of group IVb of the periodic table. The second column contains the surface tension as measured in the liquid state near the freezing point. The values of the fourth column are the parachors as derived from columns two and three. If we subtract from these values the atomic parachors deduced by Sugden[2] from the surface tension of covalent compounds and listed in column five, we obtain the data of the sixth column. These values can be interpreted as structural parachors and are indicative of the nature of bonding between the atoms of the elements in the liquid state. The increase of the structural parachor from lead to germanium in nearly equal steps is striking. Sugden assumed a structural parachor of zero for the sharing of one electron pair and derived structural parachors of 11.6 and 23.3 for the sharing of

---

* Presented at the American Physical Society meeting at Durham, North Carolina, March 26–28 (1953).

[1] See A. Weissberger, *Physical Methods of Organic Chemistry. I* (Interscience Publishers, New York, 1945).

† After completion of this paper we learned that W. D. Kingery and M. Humenik, J. Phys. Chem. **57**, 359 (1953), found 730±10 dynes/cm for the surface tension of silicon in helium, using the sessile drop method. This is in very good agreement with our results.

[2] S. Sugden, *The Parachor and Valency* (G. Routhledge and Sons, London, 1930).

two and three electron pairs, respectively. He therefore concluded that in liquid lead two pairs of electrons are shared between neighboring atoms, while in tin three pairs are shared. The value for liquid germanium then indicates that four electron pairs are being shared between neighbors. Moreover, the fact that the structural parachor of liquid silicon does not exhibit any appreciable additional increase over that of germanium is consistent with the fact that four is the maximum number of available electrons which can be shared. These results are not in disagreement with the metalic conductivity of liquid germanium[3] and the presumably metallic conductivity of liquid silicon, since only a small fraction of free electrons is sufficient to explain the conductivity in the liquid state.

The values in parentheses for carbon must be considered a speculative extrapolation.

The results derived from the parachors do not give any answer as far as the geometrical arrangement of the atoms in the liquid state is concerned. Hendus[4] has shown that in germanium the coordination number changes from four to eight upon melting. The same result should be expected for silicon. No immediate connection between these results and the values of the parachor can be expected.

TABLE I. Surface tension and parachor of the elements of group IVb.

IVb elements	Surface tension in the liquid phase dynes/cm	Atomic volume[a]	Parachor of the elements in the liquid phase	Atomic parachor from compounds[b]	Structural parachor	Sugden's values
C	(2100)	5.41	(36.8)	4.8	(32)	
Si	720	12.0	61	33–35	28–36	
Ge	600	13.5	67	38–36	29–31	
Sn	530	16.2	79–84[b]	58	21–26	23.3
Pb	450	18.3	84–91.4[b]	76.2	8–15	11.6

[a] H. D. Hubbard and W. F. Meggers, *Periodic Chart of the Atoms* (W. W. Welch Scientific Company, Chicago, 1950).

[b] See reference 2.

---

[3] R. W. Keyes, Phys. Rev. 84, 367 (1951).

[4] H. Hendus, Z. Naturforsch. 2a, 505–521 (1947).

PHYSICAL REVIEW VOLUME 91, NUMBER 3 AUGUST 1, 1953

Double Hysteresis Loop of $BaTiO_3$ at the Curie Point

WALTER J. MERZ
Bell Telephone Laboratories, Murray Hill, New Jersey

(Received April 23, 1953)

It is known that the Curie point θ of the ferroelectric $BaTiO_3$ shifts to higher temperatures when a dc bias field is applied. If the crystal shows a sharp transition, we expect by applying an ac field at the Curie temperature that the crystal would become alternately ferroelectric and nonferroelectric in the cycle of the ac field. This can be seen in the shape of the hysteresis loop at temperatures slightly above θ. In the center of the polarization P *versus* field E plot, we observe a linear behavior corresponding to the paraelectric state of $BaTiO_3$ above θ. At both high voltage ends, however, we observe a hysteresis loop corresponding to the ferroelectric state. A change in temperature causes a change in size and shape of the double hysteresis loops, ranging from a line with curves at the ends (higher temperature) to two overlapping loops (lower temperature). The results obtained allow us to calculate the different constants in the free-energy expression of Devonshire and Slater. One of the results shows that the transition is of the first order since the P^4 term turns out to be negative. The properties of the hysteresis loops are discussed, especially the large spontaneous electrical polarization and the low coercive field strength.

I. INTRODUCTION

SEVERAL investigators[1–3] have shown that the Curie point θ of $BaTiO_3$ and some other ferroelectrics[4] is displaced to higher temperatures by application of a biasing field. Having available some unusually good crystals, it has been possible to investigate their behavior at the Curie point more carefully. The crystals used had simple, well-defined domain patterns; i.e., they had only parallel and antiparallel domains.[5] They also showed very sharp transitions and were good insulators even at elevated temperatures.

By working at temperatures a few degrees above the Curie temperature, it has been possible to study the $BaTiO_3$ crystals as they change from nonferroelectric to ferroelectric and back during each cycle of a strong 60 cycle field. At zero or low values of field, the crystal is not ferroelectric, since its temperature is above the normal Curie point. But at the peak values of the field, the Curie temperature is shifted by the field, so that the crystal there is below its Curie point and displays the properties of a ferroelectric.

---

[1] A. F. Devonshire, Technical Report L/T 185 British Electrical and Allied Industries Research Associates, 1948 (unpublished).

[2] W. Kaenzig and N. Maikoff, Helv. Phys. Acta 24, 343 (1951).

[3] M. E. Caspari and W. J. Merz, Phys. Rev. 80, 1082 (1950).

[4] G. Shirane, Phys. Rev. 86, 219 (1952).

[5] W. J. Merz, Phys. Rev. 88, 421 (1952).