

Structure of Liquid As: A Peierls Distortion in a Liquid

R. Bellissent

*Laboratoire Léon Brillouin, Commissariat à l'Energie Atomique-Centre d'Etudes Nucléaires de Saclay,
F-91191 Gif sur Yvette Cedex, France*

C. Bergman

*Laboratoire de Thermodynamique et Microcalorimétrie du Centre National de la Recherche Scientifique,
F-13003 Marseille, France*

R. Ceolin

Laboratoire de Chimie-Physique, Faculté de Pharmacie, Université de Tours, F-37032 Tours Cedex, France

and

J. P. Gaspard

*Institut de Physique B5, Université de Liège, B-4000 Sart Tilman, Belgium
(Received 25 August 1986)*

A neutron-diffraction experiment ($\lambda=0.704 \text{ \AA}$) has been performed on liquid arsenic above the triple point. The coordination number ($Z=3$) does not change thru the semimetal-to-semiconductor transition on melting. This is in sharp contrast to the elemental semiconductors (Si,Ge) that undergo a semiconductor-to-metal transition upon melting, accompanied by an increase ($4 \rightarrow 6.4$) of the coordination number. The nonmetallic behavior of As, which has a half-filled p band, can be understood as a Peierls distortion in the p -bonding mechanism (three p - p bonds are reinforced; the others are considerably weakened).

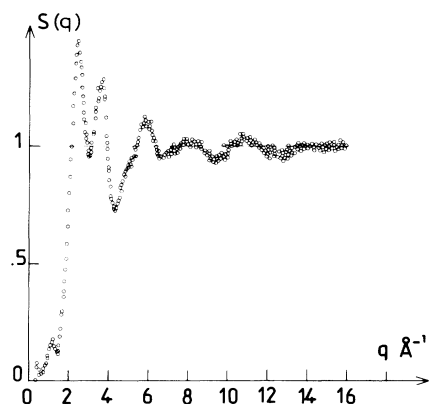
PACS numbers: 61.25.-f, 61.12.Gz

The elemental group-IV semiconductors (Si,Ge)¹ and their isoelectronic III-V compounds (InSb,² GaAs³) drastically change their structural and electronic properties upon melting: Their coordination number increases from four to six and they undergo a semiconductor-to-metal transition associated with a high value of the entropy of melting. In this paper, we show that arsenic, a group-V semimetal, has a completely different behavior as it keeps its coordination number $Z=3$ in the liquid state. Moreover liquid arsenic is semiconducting ($E_g=0.5 \text{ eV}$).

The valence three of group-V elements (P, As, Sb, and Bi) in their crystalline structures can be simply explained as the result of a Peierls distortion of p -bonded atoms. Indeed, an atom of group-V element has an electronic configuration s^2p^3 . The s level lying far below ($\approx 8.4 \text{ eV}$) the p level, the fully occupied s band in the crystal does not contribute to cohesion which is dominated by the half-filled p shell. The six lobes of the p orbitals pointing at right angles lead to a simple cubic (or related) structure. However, such a structure is unstable against doubling of the periodicity for a half-filled band. Doubling of the periodicity in the three principal directions of the simple cubic structure can be achieved by the alternation of short (covalent) bonds and long (weakly covalent) van der Waals bonds: It leads to the $A7$ rhombohedral structures for As, Sb, and Bi or to the orthorhombic structure of P and As; both structures consist of

double layers of tricoordinated atoms.⁴ In addition to a gain in the electronic energy, doubling of the periodicity opens a gap at the Fermi level. (Group-V elements are semiconductors or semimetals.) In the crystal, the opening of a gap results from the orthogonality of the dispersion relations at the Brillouin-zone boundaries. The classical explanation of the Peierls distortion mechanism requires the periodicity. In this paper, we demonstrate for the first time that a Peierls-type distortion may still exist in a liquid. Indeed, we show that the coordination number of liquid arsenic is exactly three as in the crystal; the absence of a Peierls-type distortion would have given a sixfold-coordinated structure like that of polonium at room temperature.

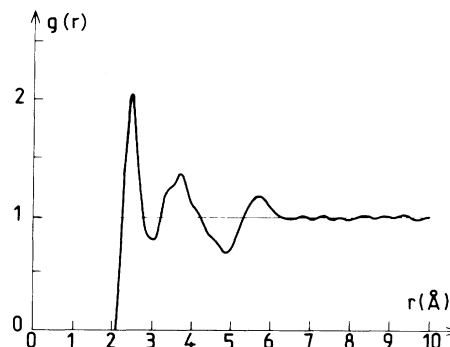
The difficulty in performing an experiment on liquid As is due to the high pressure of its triple point which prevents it from melting at atmospheric pressure. Arsenic is known to sublime around 610°C ($p=1 \text{ atm}$); its triple point lies at $p=37 \text{ atm}$ and $T=817^\circ\text{C}$. The melting of As has been achieved in a sealed amorphous cylindrical quartz container (6 mm internal diam, 1 mm thickness, and 100 mm length). The neutron-diffraction experiment has been performed on the hot source (neutron thermalized in graphite at 1400 K) of the Orphée reactor at Saclay (spectrometer 7C2⁵) with a wavelength $\lambda=0.704 \text{ \AA}$ [Cu(111) Bragg reflection]. The diffraction spectrum is recorded on a multidetector [band of 640 detectors, the aperture (angular step) of which is

FIG. 1. The interference function $S(q)$ of liquid arsenic.

0.2°]; this corresponds to a k range $0.43 \text{ \AA}^{-1} < k < 16 \text{ \AA}^{-1}$. The sample was slowly heated and then held in the liquid state at 825°C ($p=47 \text{ atm}$) in a vanadium furnace made of a vertical cylindrical sheet of 0.1 mm width, the difference of temperature between the extremities of the ampule not exceeding 3°C . The raw data are corrected the usual way: The furnace and empty-container signals are subtracted, with transmission Pallman and Pings's corrections. The data are then corrected for multiple scattering ($< 1\%$), inelasticity (Placzek, $< 1\%$), and detector efficiency. A subsequent diffraction experiment on a piece of vanadium allows us to calibrate (and renormalize) the response of all the detectors. The corrected diffraction data are shown in Fig. 1 in the k range $k < 15.5 \text{ \AA}^{-1}$. A small prepeak appears at 1.38 \AA^{-1} followed by peaks at 2.45, 3.74, 5.86, and 8.00 \AA^{-1} .

The damping of the peak heights when k increases is relatively fast, somewhat like in liquid metals. Figure 2 shows the pair correlation function $g(r)$. The first peak at $r_1=2.50 \text{ \AA}$ is well defined (at least for a liquid at high temperature). The experimental peak height (2.05) is dependent on the k range (k_{max}). [E.g., in the case of amorphous arsenic, the maximum value of $g(r)$ is 2.7 if $k_{\text{max}}=9.5 \text{ \AA}^{-1}$ and 4.6 if $k_{\text{max}}=23.5 \text{ \AA}^{-1}$.] The peak of second neighbors contains two contributions: The peak at $r'_2=3.75 \text{ \AA}$ corresponds to the six second neighbors of the crystal at 3.77 \AA while the shoulder at $r_2=3.4 \text{ \AA}$ has to be related to the interplanar nearest distance of the crystal (three neighbors at 3.15 \AA in the rhombohedral structure, 3.2 \AA and twice 3.56 \AA in the orthorhombic structure). The number of neighbors under the double peak cannot be determined with an accuracy better than one. It is between eight and nine, the crystalline value.

The angle of three covalently bonded atoms can be estimated from the ratio of the two peak positions r'_2 and r_1 . It amounts to 97° in the liquid, a value indistinguishable from the rhombohedral value (97.2°) and slightly smaller than the amorphous value (98° to 103°),^{6,7}

FIG. 2. The pair correlation function $g(r)$ of liquid arsenic.

which indicates also that the liquid structure is different from the simple cubic structure.

After the third peak at $r_3=5.7 \text{ \AA}$, there is no subsequent structure, i.e., $g(r) \cong 1$, above $r=6.5 \text{ \AA}$, a common feature in noncompact structures. Indeed, in those systems the structure is not "nested" shell by shell. Above the third shell of neighbors, the atoms are randomly distributed. This is also observed in liquid Si, Ge,¹ and GaAs,³ which are roughly hexavalent in the melt. Table I shows the values of the peak positions and coordination numbers in the crystalline (rhombohedral) amorphous and liquid arsenic. An important result is the coordination of three ($n_1=3.00$) in the melt which indicates that the Peierls distortion mechanism of the simple cubic structure survives in the liquid. It can be shown theoretically⁸ that the instability of a half-filled band (such as polyacetylene or group-V elements) has a local character and still exists in the absence of periodicity.

Let us remark that liquid As is a semiconductor as shown by the decrease of resistivity with temperature in the melt.⁹ The electrical gap is found to be $E_g=0.5 \pm 0.05 \text{ eV}$ just above T_m from the analysis of conductivity, a value intermediate between the crystalline structures [$E_g=0$ (rhombohedral) or $E_g=0.3 \text{ eV}$ (orthorhombic)] and the amorphous structures ($E_g=1.1$ to 1.4 eV). It is a very unusual situation in which the conductivity is semimetallic (or small-gap semiconducting) below T_m and semiconducting above. This has to be contrasted with Si and Ge which behave inversely while Se is semiconducting on both sides of T_m . On the other hand, Te becomes more conducting in the melt with an

TABLE I. Peak positions and coordination numbers for rhombohedral (c), amorphous (a), and liquid (l) arsenic.

| i | r_i (Å) | | | n_i | |
|---|-----------|--------|----------|-------|------|
| | c | a | l | c | l |
| 1 | 2.51 | 2.47 | 2.50 | 3 | 3.07 |
| 2 | 3.15/3.77 | ?/3.79 | 3.4/3.75 | 3+6 | 9.8 |

increase of both the coordination number ($2 \rightarrow 2.8$) and the interatomic distance ($2.87 \rightarrow 2.92 \text{ \AA}$) upon melting. By comparison, one observes that As behaves much more like Se (coordination and interatomic distances unchanged). In fact, this is just a question of temperature scale; it is likely that for group-V, -VI, and -VII elements the Peierls distortion leading to the $Z = 8 - N$ rule is destroyed by the temperature (also by pressure), so that at high temperature these p -bonded systems tend to a sixfold-coordinated structure like that of Po. It is suggested that far above T_m , As should be sixfold coordinated, Se and Te as well, but only Te shows an increased coordination number at T_m : The relevant parameter should be $\Delta E_c/kT$, the difference of cohesive energies between the Peierls-distorted and undistorted (six coordinated) structures divided by the temperature. At extremely high temperatures, a close packed ($Z \approx 10$) liquid metallic structure should appear for As with larger interatomic distances in analogy to Sb ($Z = 8.7$) and Bi ($Z = 8.8$).¹⁰

Let us remark that As has an anomalously high melting entropy (5.51 cal/mol K), three times as much as the melting entropy of metals (2 cal/mol K). It cannot be obviously attributed to an electron delocalization mechanism¹¹ such as for Si and Ge.

A structural model of liquid As has still to be constructed. As a result of our diffraction data, we suggest a model of randomly corrugated planes of tricoordinated atoms similar to the models put forward for amorphous As.⁷ Let us finally mention that models of dilated rhombohedral or (better) orthorhombic structures correctly fit

the peaks of the interference function $S(q)$ (with a suitable broadening of the interference peaks), showing again the similarities of local structures of liquid and crystalline arsenic.

Laboratoire Léon Brillouin is a Laboratoire Associé au Centre National de la Recherche Scientifique-Commissariat à l'Energie Atomique.

¹J. P. Gabathuler and S. Steeb, *Z. Naturforsch Teil A* **34**, 1314 (1979).

²H. Krebs, *Angew. Chemie* **70**, 468 (1958).

³C. Bergman, C. Bichara, P. Chieux, and J. P. Gaspard, *J. Phys. (Paris), Colloq.* **46**, C8-97 (1985).

⁴W. B. Pearson, *The Crystal Chemistry and Physics of Metals and Alloys*, (Wiley, New York, 1972).

⁵J. P. Ambroise and R. Bellissent, *Rev. Phys. Appl.* **19**, 731 (1984).

⁶R. Bellissent and G. Tourand, in *Proceedings of the Sixth International Conference on Amorphous and Liquid Semiconductors, Leningrad, 1975*, edited by V. T. Kolomiets (Nauk, Leningrad, 1976).

⁷C. N. Greaves, S. R. Elliott, and E. A. Davis, *Adv. Phys.* **20**, 49 (1979).

⁸J. P. Gaspard, A. Pellegatti, and F. Marinelli, *Europhys. Lett.* **3**, 1095 (1987).

⁹V. M. Glazow, S. N. Chizhevskaya, and N. N. Glogaleva, *Liquid Semiconductors* (Plenum, New York, 1969).

¹⁰Y. Waseda, in *Third International Conference on Liquid Metals—1976*, edited by R. Evans and D. A. Greenwood, IOP Conference Proceedings No. 30 (Institute of Physics, Bristol and London, 1977).

¹¹B. K. Chakraverty, *J. Phys. Chem. Solids* **30**, 454 (1968).