

Letters to the Editor

THE Letters to the Editor section is subdivided into three parts entitled *Communications, Comments and Errata, and Notes*. These three sections are all subject to the same limitations on length. The textual material of each Letter is limited to a number of words equal to 950 minus the following: (a) 200 words for each average-sized figure; (b) 50 words for each displayed equation; (c) 7 words for each line of table including headings and horizontal rulings. No proof will be sent to the authors of "Communications" and "Comments and Errata." Proof will be sent to the authors of "Notes." The publication charge for Letters is \$30 per page, with a minimum of \$30 per Letter. If honored, the Institution will be entitled to 100 reprints without covers. See issues of May-September, 1957, for descriptions of categories.

Communications

Formation of an Amorphous Form of Quartz under Shock Conditions

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IN order to interpret equations of state data on substances under high pressure shock conditions, it is necessary to know the phase present under shock. In a series of tests in which the samples were recovered after shock loading, an interesting change was observed in quartz single crystals.

Specimens cut from natural quartz crystals to 1 in. \times 1 in. \times $\frac{1}{4}$ in. were struck by explosively driven aluminum plates. The shock pressure was calculated to be slightly in excess of 600 kilobars. X-ray powder patterns showed the recovered fragments to be amorphous. These fragments had a density of 2.22 g/cc and were optically isotropic, $n=1.46$. The fragments were either milky-white or transparent and showed moderate fluorescence under uv illumination. The temperature of the quartz was calculated to be no greater than 1400 °K during shock, and no greater than 1000 °K immediately after the shock.

Similar specimens were explosively loaded to calculated pressures of 350 kilobars. The fragments were milky in appearance, but the x-ray powder patterns showed broadened lines of alpha quartz. These fragments had densities of approximately 2.64.

Quartz crystals, $\frac{1}{4}$ in. in diameter and $\frac{3}{8}$ in. long, were traversed by the mach disc region of a cylindrically converging shock wave. The pressure in this region was a calculated 360 kilobars. The crystals were frequently recovered almost whole, showing original crystal faces and terminations. The index of refraction, density,

fluorescence, and x-ray powder pattern of this material were the same as the fragments recovered from the 600 kilobar tests, i.e. an amorphous form of SiO₂.

In further experiments, $\frac{1}{2}$ -in. diameter cylindrical crystals were loaded by a cylindrically converging shock. The mach disc pressure was again 360 kilobars, confined to a region of radius 0.09 in. Outside this region the pressure fell away to 170 kilobars. These specimens were amorphous in the center, crystalline outside the mach disc region.

For a pressure of 360 kilobars, the temperature of the quartz was calculated to be at most 870 °K. This reduced after shock passage to 515 °K. To make the pressure-temperature calculations, Bridgman's data¹ for the compression of quartz and fused quartz to 100 kilobars were analytically fitted to the Murnaghan equation²

$$1+rP/k=(P/P_0)^r.$$

The constants determined were, quartz, $r=8.509$ and $k/r=0.04353$ megabars; fused quartz, $r=5.5977$ and $k/r=0.03993$ megabars.

There are a number of possible explanations for the formation of amorphous material from single crystals in these experiments.

(1) Although hydrodynamic theory has been successfully applied to the explanation of a variety of effects associated with the passage of intense shock waves through solids, the theory may not fit the case of quartz. Hence the pressure and temperature calculations may be in error and the phenomenon observed was simply fusion under lower pressures and higher temperatures than those calculated.

(2) If a great many dislocations are formed in the shock front, the reversion of the disordered state to crystallinity may be mechanically impossible. This explanation may be related to the disordering of quartz by neutron bombardment.³

(3) Alpha (or beta) quartz may melt metastably at temperatures well below the melting point of the stable form of SiO₂. This last hypothesis is supported at least qualitatively by current data.

It should be noted that under the pressure and temperature conditions of these experiments alpha quartz is unstable with respect to coesite.⁴ However under static conditions at 400 °C, this transformation is sluggish and it probably would not have time to take place during shock. Therefore under transient high pressures quartz which is metastable itself may transform to another metastable state. Such transformations have been previously demonstrated in CaCO₃⁵ under static high pressures.

A simple use of the Murnaghan fits for quartz and fused quartz indicates that above 600 kilobars the glass is more dense than the crystalline material. However, Bridgman and Simon⁶ report formation of glasses with densities up to 2.61 after compression by pressures of

200 kilobars. These results suggest that the extrapolation past 100 kilobars of the Murnaghan equation for fused silica is not good. It is therefore not impossible that a glass becomes the denser phase at considerably less than the predicted 600 kilobars. In this case, the formation of a glass in these experiments is thermodynamically possible although the glass itself is metastable with respect to coesite. The glass is preserved after shock by the sluggishness of the recrystallization process.

This glassy transition is apparently not peculiar to quartz. In another experiment, an albite ($\text{NaAlSi}_3\text{O}_8$) crystal was transformed to a glass by an over 600 kilobar shock.

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¹ P. W. Bridgman, Proc. Am. Acad. Arts and Sci. **76**, 68 (1948).

² F. D. Murnaghan, *Finite Deformation of an Elastic Solid* (John Wiley & Sons, Inc., New York, 1951).

³ See, for example, W. Primak, Phys. Rev. **110**, 1240 (1958).

⁴ G. J. F. Mac Donald, Am. J. Sci. **254**, 713 (1956).

⁵ J. C. Jamieson, J. Geol. **65**, 334 (1957).

⁶ P. W. Bridgman and I. Simon, J. Appl. Phys. **24**, 405 (1935).

Structure of Tetracobaltdodecarbonyl

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TETRACOBALTDODECARBONYL, whose structural determination we have undertaken, crystallizes in the rhombic system with the following unit cell constants: $a = 11.66 \pm 0.07$ Å, $b = 8.94 \pm 0.05$ Å, $c = 17.14 \pm 0.10$ Å, $N = 4$, space group $Pccn$.

The Patterson projections along the three axes may be interpreted by supposing that cobalt atoms are disposed at the vertices of a regular tetrahedron with

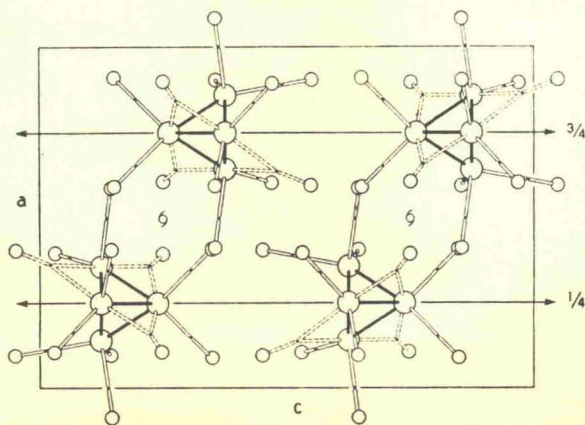


FIG. 1. Projection of the structure on (010), showing the icosahedral arrangement of oxygen atoms within each molecule. Vicariant molecules around the twofold axes $(\frac{1}{2}, \frac{1}{2}, z)$ and $(\frac{3}{4}, \frac{3}{4}, z)$ are not drawn.

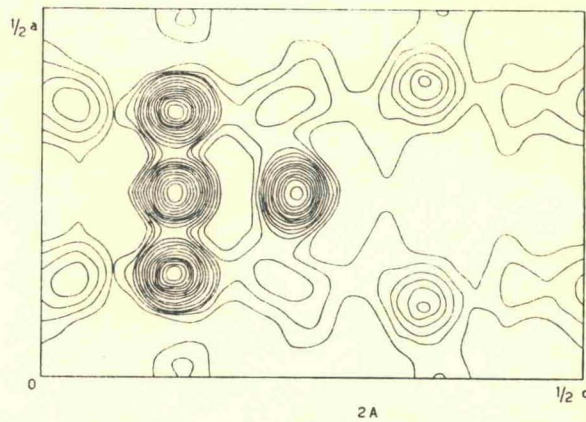


FIG. 2. Preliminary Fourier projection of the electron density on (010). Levels every 4, 6, 8, ... $e/\text{Å}^2$.

fractional coordinates:

	x	y	z
Co(I)	0.250	0.411	0.122
Co(II)	0.358	0.168	0.122
Co(III)	0.142	0.168	0.122
Co(IV)	0.250	0.250	0.240

The cobalt-cobalt distances are 2.50 ± 0.05 Å compared with the value (2.54 Å) quoted for $\text{Co}_2(\text{CO})_8$.¹

The twofold axis $(\frac{1}{2}, \frac{1}{2}, z)$ passes through Co(IV) perpendicularly to the equilateral triangle Co(I)—Co(II)—Co(III) so that statistical vicariance of differently oriented molecules occurs in each site of the crystal, in a manner similar to that described in this journal for $\text{Fe}_3(\text{CO})_{12}$.²

From preliminary Fourier projections along the three axes, it is found, moreover, that oxygen atoms are approximately disposed at the vertices of a regular icosahedron, with an edge of about 4.1 Å. A twofold axis of the icosahedron coincides with the twofold axis $(\frac{1}{2}, \frac{1}{2}, z)$ so that the encumbrance of vicariant molecules is the same as far as it is due to oxygen atoms.

The only possible model of structure, for which the positions found for oxygen and cobalt atoms correlate with reasonable requirements of stereochemical character, is shown projected on the ac plane, in Fig. 1. The corresponding preliminary Fourier projection is shown in Fig. 2. The molecule possesses a noncrystallographic

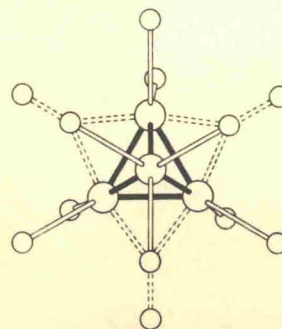


FIG. 3. Model of the molecule of $\text{Co}_4(\text{CO})_{12}$ viewed down the threefold (noncrystallographic) symmetry axis.