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NEW PHASES AND CHEMICAL REACTIONS IN SOLID CO UNDER PRESSURE

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Résumé - Nous avons déterminé le diagramme de phase du monoxyde de carbone par diffraction des rayons X et spectroscopie Raman, de 15 à 297 K et à des pressions de 1.0 à 10.0 GPa. A basse température et au voisinage de 3.4 GPa, la phase connue α (groupe d'espace $P2_13$) se transforme en une phase nouvelle ε (de structure inconnue), au lieu de la phase prévue γ ($P4_2/mnm$). Nous avons trouvé une transformation de CO - β (groupe d'espace $P6_3/mmc$) en une phase nouvelle δ (Pm3n), au voisinage de 5.2 GPa, à la température ambiante. Au-dessus de 4.6 GPa et 80 K, environ, lorsque irradié par lumière visible laser, CO subit une réaction photochimique. Cette tendance à réagir peut être associée avec la formation d'un polymère jaune qui subsiste jusqu' à pression nulle. Des mesures ESCA indiquent que le polymère est composé de sous-oxyde de carbone $(C_3O_2)_x$.

Abstract - The phase diagram of solid carbon monoxide was determined by x-ray diffraction and Raman spectroscopy from 15 to 297 K at pressures from 1.0 to 10.0 GPa. At low temperature a transition occurs near 3.4 GPa from the known α-phase (space group $P2_13$) to a new ε-phase (structure unknown), rather than to the predicted γ-phase ($P4_2/mnm$). A transformation from β-CO (space group $P6_3/mmc$) into a new δ-phase (Pm3n) was found near 5.2 GPa at room temperature. Above about 4.6 GPa and 80 K, CO reacts photochemically when irradiated with visible laser light. The photoreactivity may be associated with the formation of a yellow polymer, which can be recovered at zero pressure. ESCA measurements indicate that the polymer is composed of carbon suboxide $(C_3O_2)_x$.

I. INTRODUCTION

The gases CO and N_2 are close molecular analogues. At low pressure they condense into liquids with almost identical molar volumes and freeze into solids with similar crystal structures. Recently [1] the phase diagram of N_2 was determined by Raman spectroscopy from 15 to 300 K at pressures to 52 GPa. The present study was carried out to establish the P-T diagram of the solid phases of CO over the range 15-300 K and 1.0 - 10.0 GPa using x-ray diffraction and Raman spectroscopy. Although we find similarities in the physical structures of the high-pressure forms of solid CO and N_2, there are striking differences in chemical behavior. Above about 4.6 GPa and 80 K, CO forms a yellow solid that can be recovered at zero pressure. Chemical analysis indicates that the solid may be a mixture of $(C_3O_2)_x$ and other products resulting from chemical disproportionation [2].

II. EXPERIMENTAL APPARATUS AND PROCEDURE

Raman spectra were measured in a Merrill-Bassett [3] cell, loaded with 99.95% pure liquid CO by the indium-dam technique [4]. Cell temperatures from 15 to 300 K were controlled to ± 1 K by a helium-flow cryostat. We calculated pressures using the frequency shift of laser-induced fluorescence from ruby powder in the cell [1,5,6]. Both the ruby fluorescence and Raman spectra were measured with a Spex 1403 spectrometer using Kr^+ 15454-cm^{-1} laser radiation.

Our x-ray studies of solid CO were carried out in a Be gasket clamped between tungsten-carbide anvils in a hydraulic press [7]. A collimated beam of Cu K_α radiation was directed through the gasket, and the diffracted x rays were photographed with a 114.6-mm diam. powder camera. We attained temperatures between 100 and 300 K by circulating liquid nitrogen through the press platens. Pressures were determined from diffraction lines of <u>in situ</u> NaF, the compression of which is known from shockwave experiments [8].

In order to synthesize a sufficient amount of CO-disproportionation product for chemical analysis, we modified the x-ray apparatus by incorporating a larger volume gasket (~0.5 mm^3) made of BeCu, stainless steel, or Inconel. The anvils and gasket were also enclosed by a metal bellows, equipped with a capillary line and sealed against the platens with indium rings. This arrangement allowed the gasket to be filled with liquid CO before pressurization and to be emptied into a mass spectrometer for analysis of product after pressurization. Pressures were applied for up to 100 h, while the platens and cell were electrically heated to 345 K.

III. RESULTS AND DISCUSSION

Raman spectra, characteristic of the vibron regions of α-, β-, δ-, and ε-CO and of the lattice-mode regions of α-CO and ε-CO, along with the Raman frequencies as a function of pressure have already been published [2]. From our present extension of this work we can now construct the phase diagram for CO, shown in Fig. 1. The open symbols represent Raman observations and the closed ones represent corroborating x-ray data. Coincident symbols in Fig. 1 signify phase boundaries. The space groups of the various crystal phases have been reported as α-CO ($P2_13$) [9], β-CO ($P6_3/mmc$) [10,11], and δ-CO (Pm3n) [2]. Our results confirm these structures. The α, β, and δ forms have analogues in the N_2 phase diagram [1], which exhibits an additional γ phase ($P4_2/mnm$) [12,13], not seen in CO, possibly because of its much larger quadrupole interaction energy [14].

Our calculated and observed interplanar spacings, and observed intensities for ε-CO at 6.9 GPa and 100 K are given in Table I. The diffraction pattern can be indexed as rhombohedral with a = 5.96 Å and α = 85.7°. If it is assumed that there are eight CO molecules per primitive unit cell, the molar volume has the reasonable value 16.0 cm^3. The structure appears to be a small rhombohedral distortion of cubic δ-CO (Pm3n). The three strongest diffraction lines in the cubic (Pm3n) structure of δ-CO or δ-N_2 are the (200), (201), and (211), while the other low index powder diffraction lines are unobservable. This situation carries over to rhombohedral ε-CO where the (200); (201), $(20\bar{1})$; (211), $(21\bar{1})$, and $(2\bar{1}\bar{1})$ are the

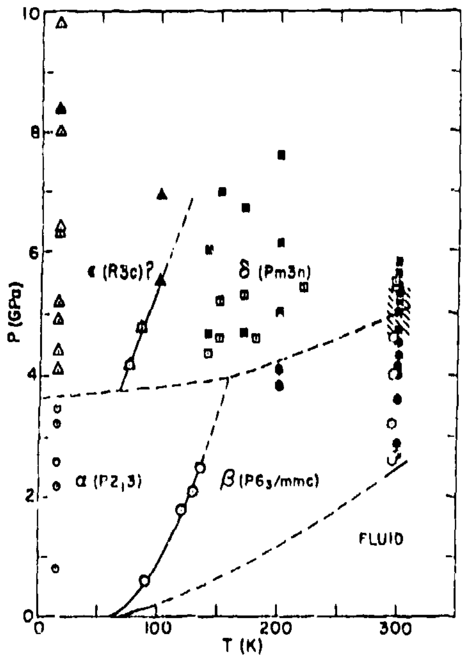

Fig. 1. Phase diagram of condensed CO. Open symbols, Raman observations; closed symbols, x-ray determinations; circle, α-CO ($P2_13$); hexagon, β-CO ($P6_3/mmc$); square, δ-CO ($Pm3n$); triangle, ε-CO ($R3c$)?; solid line, established phase line; dashed line, estimated phase line; cross hatch, region where both β-CO and δ-CO were observed. Coincident points indicate coexisting phases.

Table I. Calculated and observed interplanar spacings and reflected intensities for ε-CO at 6.9 GPa and 100 K.

hkl (rhomb.)	d_{calc} (Å)	d_{obs} (Å)	I
200	2.978	2.982	8
201	2.741	2.733	6
$20\bar{1}$	2.592	2.587	10
211	2.585	2.587	
$21\bar{1}$	2.404	2.399	10
$2\bar{1}\bar{1}$	2.351	2.351	2
220	2.183	2.182	4

first strong lines. The space group cannot be uniquely determined from the present data, but it is most likely R3c if the molecules exhibit head-to-tail order or $R\bar{3}c$ if they are disordered.

When CO is pressurized above about 4.6 GPa at temperatures greater than 80 K, chemical disproportionation can occur, resulting in a solid product that persists when the pressure is removed. Induction of the chemical reaction depends on temperature, elapsed time, and exposure to visible laser light or x rays. These factors also affect the color of the solid, which varies from light yellow to dark red, and its consistency, which varies from fine-grained to caramel-like. All of the samples appeared quite porous and, indeed, the total amount of solid produced corresponded to only about 5-10% of the initial CO charge. The solid samples were soluble in water, acetone, and alcohol and were degraded by air and light.

ESCA (Electron Spectroscopy for Chemical Analysis) measurements showed that the solid product contained carboxylated carbon atoms and graphitic carbon atoms. On this basis, and from the similarity of our product to poly-carbon-suboxide $(C_3O_2)_x$ prepared chemically at 1 bar [15-19], we believe that we have synthesized this material from CO alone under pressure. It was first assumed that CO might undergo chemical disproportionation in the pressure cell according to

$$4\ CO \xrightarrow{P} C_3O_2 + CO_2, \qquad (1)$$

and

$$x\ C_3O_2 \rightarrow (C_3O_2)_x \quad . \qquad (2)$$

However, mass spectrometric analysis of the gas released from the cell after pressurization showed only unreacted CO, with no trace of CO_2. Furthermore, x-ray diffraction photographs of the solid gave a sharp pattern which must be associated with a second, crystalline product.

We now speculate that the reaction may proceed as

$$5\ CO \xrightarrow{P} C_3O_2 + C_2O_3 \qquad (3)$$

followed by polymerization of C_3O_2 and possibly by

$$2\ C_2O_3 \rightarrow (C_2O_3)_2 \qquad (4)$$

where $(C_2O_3)_2$ is a dimer of oxalic anhydride. Additional studies aimed at measuring far IR absorption, x-ray structure, electron spin concentration, and decomposition products are currently underway.

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