Neutron diffraction study of crystal structure and temperature driven molecular reorientation in solid α-CO

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ABSTRACT
Neutron diffraction studies have been carried out on carbon monoxide (CO) in the temperature range of 14–68 K. From the data of the temperature dependent crystal parameters, the volume thermal expansion $\beta$ (T), C–O bond length, and intermolecular distance of CO have been determined and compared with calculations. The volume evolution of cubic CO solids indicates a normal thermal expansion. However, the bond length of CO molecules contracts with the increase in temperature. Correspondingly, the distance between CO molecules increases much faster with an increase in the temperature. We find that intermolecular and intramolecular interactions account for these abnormal temperature behaviors of CO molecular crystals. The abnormal change observed in the curve $\beta$ (T), evolution of C–O bond length, and distance between two CO molecules indicate an order–disorder phase transition induced by head-to-tail reorientations of CO dipoles.

INTRODUCTION
Carbon monoxide (CO) is the second most abundant gas after H$_2$ in the universe and is a common solid molecule found in the interstellar medium and solar system ice. It has been reported that more than half of the atmospheric CO came from anthropogenic sources. Disturbance in the CO amount will perturb tropospheric chemistry, resulting in global warming and other climatic changes. Recently, the Planck space telescope made available the first-ever all-sky map of carbon monoxide in the cosmos, which can help spot star-forming regions where carbon monoxide glows brightly. CO occurs in mixed gas hydrates (CO$_2$, H$_2$, N$_2$, etc.), and the formation of these phases may play an important role in comets and the outer planets in the solar system.

The CO molecule is isoelectronic with N$_2$, in which C and O atoms are connected by a triple bond. It consists of two regular covalent bonds and one dative covalent bond, which is also known as a dipolar bond or coordinate bond. At low temperature, CO condenses into liquid and then freezes at triple points of 68.15 K, forming a disordered hexagonal solid β-phase. When cooled down to 61.6 K, the solid β-phase will transform to a molecular ordered α-phase. The primitive structure of α-CO is cubic, with a basis of four molecules per unit cell, and belongs either to the space group P2$_1$3 or to the space group Pa3 (similarly to N$_2$); the evidence is conflicting. According to Refs. 7–9, solid α-CO occupies centrosymmetric positions and has been assigned a disordered structure in the space group P2$_1$3 (analogous to the structure of α-N$_2$). Its molecular axes are aligned parallel to the cell diagonals. These authors reject the space group P2$_1$3 of a lower symmetry in which the molecular axes are directed along the four cube body diagonals and α-CO only slightly shifts from the Pa3 arrangement. It is worth noting here that CO is a polar molecule. The
crystal structure of the location of the molecules and the end-to-
end ordering in α-CO are related to dipolar ordering. In other
words, α-CO in its equilibrium state is bound to have the P213 struc-
ture, which differs from the Pa3 structure in which α-CO mole-
cules are in end-to-end ordering. Until now, by x-ray diffraction ex-
periments, there is no strong evidence to confirm the structure of α-CO
belonging to P213 or Pa3. More accurate measurements would be
desirable.

In this study, in order to resolve the ambiguity about the low-
temperature modification structure of solid CO, we performed a
neutron diffraction experiment by condensing CO gas in a vana-
dium gas cell under a pressure of 20 MPa at the beamline of High-
Pressure-Preferred Orientation (HIPPO), Los Alamos Neutron
Science Center (LANSCE). The temperature dependence of lattice
parameters, bond length of carbon and oxygen, and intermolecular
distance have also been investigated, which allow for the calculation
of the thermal expansion coefficient and analysis of intermolecular
and intramolecular interactions.

EXPERIMENTS

The neutron diffraction experiment was performed using Dis-
pex in a low-temperature environment, the whole chamber of
which was vacuumed to 10⁻⁵ Pa; the CO gas was loaded in a high-
pressure vanadium cell, which was previously flushed by pure CO
gas (from Alpha Asia) and vacuumed 3–4 times. Then, the CO was
pressurized up to 20 MPa at room temperature and cooled down to
the lowest temperature of 10 K. At each temperature point, for every
1–2 h, neutron exposure was collected for a better signal/noise ratio.
The neutron diffraction patterns under different temperatures were
analyzed with Rietveld refinement using the GSAS program.

Based on density functional theory (DFT) as implemented in
the Vienna Ab initio Simulation Package, first-principles cal-
culations were performed by using the projector augmented wave
(PAW) method. The electronic exchange-correlation effects
were described by local-density approximation (LDA). We chose
LDA instead of GGA because the C–O bond length in the CO gas
phase calculated by LDA (1.1351 Å) was closer to the experimen-
tal value (~1.13 Å), and the GGA result (1.1433 Å) was observably
larger. The energy cutoff of 500 eV was used for the plane wave
basis set, and a Monkhorst–Pack k-point of 6 × 6 × 6 was used for
Brillouin zone sampling. In structural relaxations, the convergence
criteria of energy and force were set to 1 × 10⁻⁵ eV and 0.02 eV/Å,
respectively. α-CO is a molecular crystal, so van der Waals (vdW)
interaction may play an important role. Here, we have used van der
Waals correction of the DFT-D3 method. Besides, all the calcula-
tions were carried out below 20 MPa, which was consistent with the
experimental conditions.

For molecular dynamics (MD) simulations, we have used an
NPT ensemble established in a supercell of 3 × 3 × 3 α-molecular
 crystal with 216 atoms in total, and only gamma point was used in
the MD simulations. During simulations, we have increased the tem-
perature from 1 K to 60 K with a step of 5 K. The time step at each
temperature was 1 fs, running for a period of 6 ps. After reaching
equilibrium, the volume and C–O bond length were averaged for
the last 3000–6000 structures at each temperature, and the error bars
were estimated by the standard deviations during statistics.

RESULTS AND DISCUSSION

Low-temperature neutron diffraction studies have been car-
ried out on carbon monoxide in the temperature range of 14–68 K.
Figure 1 shows the refined neutron diffraction patterns selected at
different temperatures. It is observed that the neutron diffraction
peaks could be well indexed with the cubic P213 unit cell in the tem-
perature range from 14 K to 60 K and with a = 5.6341(1) Å at 30 K
[as shown in Fig. 1(a)] and the hexagonal P6₃/mmc unit cell with a
= 4.1132(1) Å and c = 6.7118(3) Å at 65 K [as shown in Fig. 1(b)].

![Figure 1](https://scitation.aip.org/content/aip/journal/adv/10/4/10.1063/1.5121337)
The analysis of neutron diffraction patterns has shown that the α-CO structure belongs to the space group $P_2_13$ instead of the conflictual $Pa_3$. It is reasonable that CO has a molecular dipole compared with the $N_2$ molecule, so a slightly lower symmetric space group can be adopted for CO. More specifically, if we make a relative shift ($1/4, 1/4, 1/4$) of the two-unit cell of CO and $N_2$, along the $(111)$ direction, the intermediate $N_2$ and CO have the same orientation and almost overlapped with each other, while the upper and lower three-fold molecule rotated about $70\degree$ (as shown in Fig. 2). Another feature is that the CO molecule in the middle is with oxygen downward and the rest of the upper and lower CO molecules is with oxygen upward, in the purpose of minimizing electric polarization and total energy.

The temperature depending lattice parameter of α-CO is permitted to estimate the thermal expansion coefficients of the crystal in a wide temperature range. The values of volume and volume thermal expansion are given in Table I and are shown in Fig. 3. The profile of the temperature dependence curve $\beta(T)$ is quite typical of the ordered phase for many molecular crystals.\(^{28}\) It can be seen that the curve $\beta(T)$ undergoes an abnormal change at around 35 K, which may be related to an order–disorder phase transition induced by head-to-tail reorientations of CO dipoles.\(^{29,30}\) The mechanism of reorientation involves $180\degree$ reorientation (head–tail flips). As Li\(^{29,30}\) suggested, the CO molecules are in a disordered state for $T \geq 37$ K, in which there are head–tail disordering motions. The disordering motions are fast in the temperature range above 37 K. Below this temperature, the motions were gradually frozen as thermal fluctuation decreased. Therefore, the curve $\beta(T)$ shows a dome shape in the disordered state due to the influence of head–tail orientational disordering on the expansion.

### Table I. The lattice parameter, volume, and volume thermal expansion of α-CO as a function of temperature.

| Temperature (K) | $a$ (Å)  | $V$ (Å$^3$)  | Volume thermal expansion ($\times 10^{-4}$ K$^{-1}$) |
|-----------------|---------|--------------|-----------------------------------------------|
| 14              | 5.6357  | 178.996      | . . .                                         |
| 20              | 5.64021 | 179.426      | 4.0038                                       |
| 25              | 5.64609 | 179.988      | 6.2644                                       |
| 30              | 5.65337 | 180.685      | 7.7449                                       |
| 35              | 5.66598 | 181.897      | 13.4156                                      |
| 40              | 5.67658 | 182.919      | 11.2371                                      |
| 45              | 5.68394 | 183.632      | 7.7958                                       |
| 50              | 5.69702 | 184.903      | 13.8429                                      |
| 52.5            | 5.7039  | 185.573      | 14.4941                                      |
| 55              | 5.71182 | 186.347      | 16.6834                                      |
| 57.5            | 5.72035 | 187.184      | 17.9665                                      |
| 60              | 5.72978 | 188.111      | 19.8094                                      |
| 62.5            | 5.74099 | 189.217      | 23.5180                                      |

FIG. 2. Two unit cells of CO in $P_2_13$ and $N_2$ in $Pa_3$ crystal structures, the CO layer was shifted ($1/4, 1/4, 1/4$) relatively to the $N_2$ layer. The balls in blue, in soil color and in red represent nitrogen atoms, carbon atoms and oxygen atoms respectively.

FIG. 3. Temperature dependence of volume thermal expansion coefficient and volume of α-CO.
Figure 4 shows evolutions of the CO bond length and inter-molecular distance of solid CO as a function of temperature. It is found that the distance between CO molecules increases with rising temperature, which can be interpreted as volume thermal expansion (as shown in Fig. 3). However, the bond length of CO is contrary to the trend in intermolecular distance with increasing temperature, which indicates the decrease in intermolecular interaction between carbon and oxygen atoms. Intermolecular and intramolecular interactions play important roles in the abnormal temperature behavior of CO molecular crystals. In solid α-CO, there are three primary interactions between two carbon monoxide molecules: an attractive van der Waals interaction, a repulsive short-range interaction, and a quadrupole–quadrupole electrostatic interaction. These three intermolecular interactions were weakened due to thermal expansion; correspondingly, the interaction between C and O atoms should be enhanced to equilibrium. Therefore, intermolecular and intramolecular interactions play important roles in the abnormal temperature behavior of CO molecular crystals. It is worth mentioning that in the temperature range above 30 K, both C–O bond length and intermolecular distance show a fast change, which may be attributed to head–tail orientational disordering.

To further understand the abnormal temperature behavior of α-CO, DFT calculations were performed. As shown in Figs. 5(a) and 5(b), the average of volume and C–O bond length with the change in temperature are fluctuating, but the trend agrees well with our experiment. The reason for the fluctuation might be related to the size limitation of the supercell used in our MD simulations. From the two black solid curves shown in Fig. 5, we can see that their overall trends are consistent with the experimental results, where the volume increases as there is an increase in temperature, but the C–O bond length decreases with increasing temperature. The reason for volume expansion is easy to be understood. As for the decrease in the C–O bond length, we infer that as the temperature increases, the volume increases, leading to a weaker intermolecular van der Waals interaction. As a result, the C–O bond in the molecular crystal evolves toward the gas phase (the bond length is 1.1351 Å using LDA), so the intramolecular C–O bond length will gradually decrease.

CONCLUSIONS

In conclusion, the neutron diffraction experiment on solid CO molecules was investigated in the temperature range of 14–68 K. The structure of solid α-CO has been identified as P2_1_3, which differs from the Pa3 structure in which CO has a molecular dipole compared with N_2 molecules. The lattice parameter, volume, volume thermal expansion β (T), temperature dependence of C–O bond length, and intermolecular distance were obtained by refined high quality neutron diffraction data. The abnormal change appearing at around 30–35 K in β (T) indicates that the crystal α-CO undergoes an order–disorder phase transition induced by head-to-tail
reorientations of the CO dipoles. According to experimental data and theoretical calculation, as the temperature increases, the volume increases, but the C–O bond length decreases. This anomalous behavior of the C–O bond length with respect to increase in temperature attributes to the equilibrium between the intermolecular van der Waals interaction and intramolecular interaction between C and O atoms in CO molecular crystals.

**AUTHOR’S CONTRIBUTIONS**

L.W. and C.S. contributed equally to this work.

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