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ANOMALY IN THE HEAT CAPACITY OF CRYSTALLINE CARBON MONOXIDE AT 18 K ASSOCIATED WITH ORIENTATIONAL ORDERING

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A small anomaly in heat capacity appeared at about 18 K when α-carbon monoxide was annealed at 15-16 K for 20-40 hours. A relaxation phenomenon was observed between 14 and 19 K. The results were tentatively interpreted as due to a glass transition arising from freezing of molecular head-to-tail reorientation.

While examining the heat capacity of crystalline carbon monoxide at low temperatures, we found an anomaly that is believed to be a glass transition.

Recent calorimetric investigation on hexagonal ice(1) suggested the existence of a novel type of glassy crystal which possesses frozen positional disorder in an otherwise regular crystal lattice. There would then be a possibility of attaining perfect thermal equilibrium in ice removing all the residual entropy at temperatures above 0 K, had one waited an astronomical length of time.

Carbon monoxide is one of such crystals that possess a residual entropy arising from some frozen disorder. Its residual entropy of 4.4 $JK^{-1}mol^{-1}$ reported by Clayton and Giauque(2) has been interpreted as being due to failure of establishing equilibrium with respect to molecular head-and-tail orientation. Later measurements of the heat capacity(3-5) found no phase transitions below 14 K, the lowest temperature covered by Clayton and Giauque.

Upon re-examination of the published heat capacity curves of α-CO in the region below 20 K(6), we found a barely discernible anomaly at about 18 K. There was, therefore, a possibility that previous measurements either overlooked a 'hidden' phase transition, such as observed in solid methane at 8 K(7), or could get hold of an indication of a glass transition without being aware of the effect. The former possibility was discussed by Melhuish and Scott(8) when they calculated interactions between molecular dipoles to obtain the Curie temperature of 5 K and the latter possibility by Pitzer, et al(9) who calculated the kinetics of ordering in head-and-tail orientation.

Such circumstances prompted us to redetermine the heat capacities of α-CO below 20 K and to do some annealing experiments. Particular attention has been focused on the drift of temperature after the energy input was off in the adiabatic calorimetry because a relaxation effect was expected to occur in the neighborhood of the concealed thermal anomaly. Figure 1 shows a plot of average drift rates after 10-20 min as a function of temperature. Below 14 K and above 19 K, the thermal equilibrium was attained within ten minutes but between 14 and 19 K a temperature drift continued longer. When the specimen was cooled from 25 to 10 K in about 30 min , a warm drift (heat evolution) was observed (series 1 of Fig. 1) upon reheating to above 15 K. On

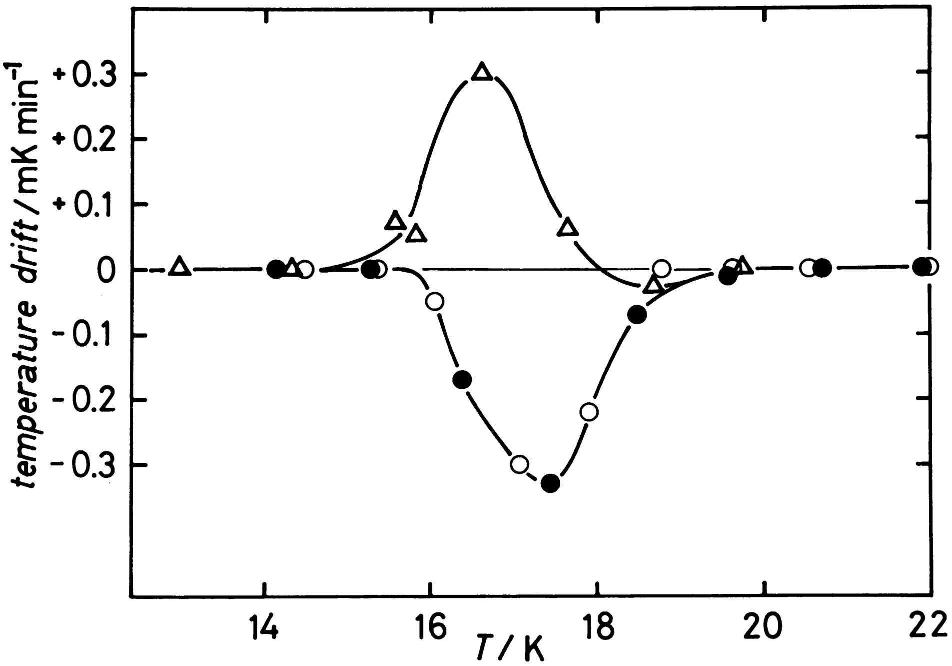

Fig. 1 Relaxation as seen by the temperature drift. △ series 1 (quenched), ● series 2 (annealed at 16 K for 19 h), ○ series 3 (annealed at 15 K for 39 h).

the other hand, a cold drift was observed when the specimen was annealed at 15.79 K for 19 hours (series 2) or at 14.95 K for 39 hours (series 3) before the heat capacity measurements were started. To compute the apparent heat capacities between 14 and 19 K, the warm drift was treated as if it were a heat leakage. However, the cold drift was taken into account by using the temperature measured after 20-30 min when the drift became very small. Fig. 2 is the result of such computation; C_pT^{-3} is plotted as a function of T to make the anomaly appear prominent. The effect of annealing is such that the heat capacity anomaly becomes larger and its maximum is displaced to lower temperature. The excess entropy associated with the anomaly is only 0.04 and 0.03 $JK^{-1}mol^{-1}$ for series 2 and 3, respectively.

All the experimental evidences seem to point to the possibility that the anomaly is due to a glass transition and the glass transition temperature T_g lies somewhere around 18 K. A glass transition is usually observed when a liquid is undercooled to the extent that motion of certain degrees of freedom becomes frozen in owing to lack of kinetic energy to attain internal thermal equilibrium. It now takes place in a stable crystal of carbon monoxide. The facts that there is no relaxation phenomenon

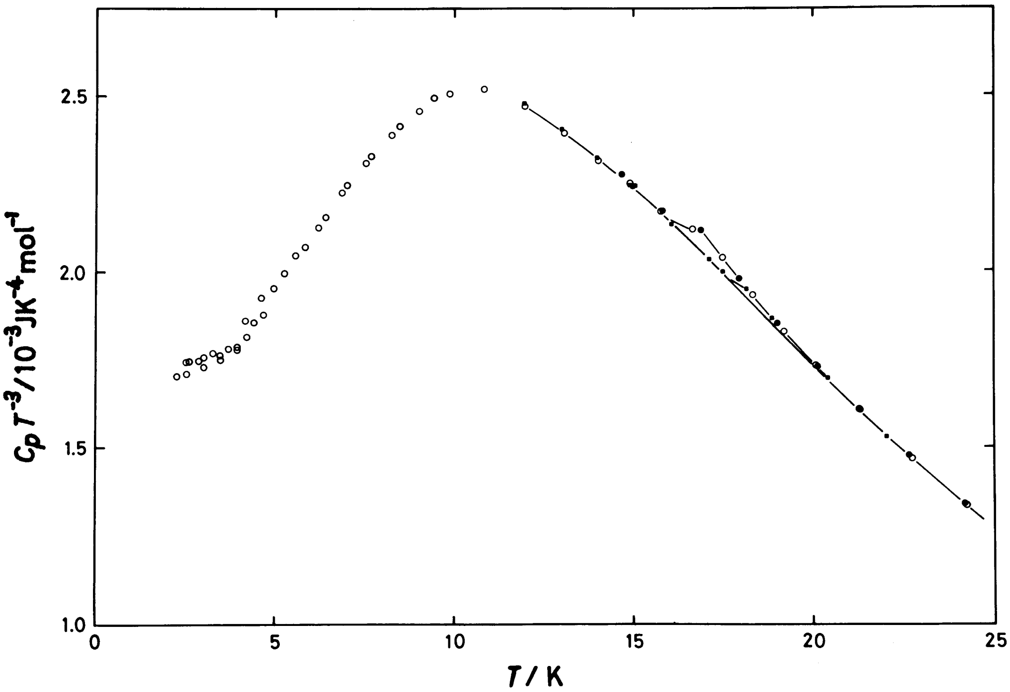

Fig. 2 Effect of annealing treatments on the heat capacity of α-CO.
■ series 1 (quenched), ● series 2 (annealed at 16 K for 19 h),
○ series 3 (annealed at 15 K for 39 h).

above 19 K and that the heat capacity above 19 K is quite reproducible irrespective of the annealing or quenching treatment show that we are looking at the equilibrium state above 19 K. Below 19 K, some degrees of freedom of motion become gradually frozen in: we assume, in the absence of direct experimental evidence, that it is the molecular tip-over degree of freedom that is frozen.

Let us consider that part of the entropy which is associated with the head-and-tail configuration. Let $S(T)$ denote such entropy a hypothetical crystal would have at the temperature T if perfect internal equilibrium were achieved. Thus $S(0)$ is zero at 0 K and would increase with temperature until S reaches $R\ln 2 = 5.76$ JK^{-1}mol^{-1} at 61.6 K, the transition point. The non-equilibrium crystal actually has $S^*(T)$ which varies very little below T_g i.e. $S^*(T)$ is almost equal to $S(T_g)$ when $T \leqq T_g$.

Now, the relaxation effect of Fig. 1 may be interpreted in the following way. When the crystal is quenched from above T_g to a temperature T_1 far below the glass transition region, $S^*(T_1)$ is almost equal to $S(T_g)$. Upon heating the crystal to a temperature T_2 which is close to T_g, the crystal in the glassy state (glassy crystal) tends to be stabilized. The stabilization process would accompany with it a decrease in entropy from $S^*(T_1)$ to $S(T_2)$, thus evolving some heat into the lattice. This situation corresponds to the experiments of series 1. On the other hand, if the crystal is quenched from above T_g to a temperature T_3 where annealing can take place in a reasonably short duration of time, the annealing process is accompanied with an entropy decrease from $S^*(T_3)$ to $S(T_3)$. Upon heating the annealed crystal to T_2, an entropy increase occurs from $S(T_3)$ to $S(T_2)$ almost isothermally, thus absorbing some heat from the lattice (cold drift). This situation corresponds to the experiments of series 2 and 3. The interpretation in terms of a glass transition phenomenon suggests that the ordering of molecular head-and-tail may take place not by a cooperative process but by a continuous change all the way from 61.6 K to 0 K.

The experimental results of the present study does not entirely exclude other interpretations. For instance, the anomaly may be associated with beginning of an order-disorder phase transition.

Further investigation into this anomaly is being undertaken.

Experimental

High purity carbon monoxide contained in 1 dm^3 bomb under 7.5 MPa was purchased from Takachiho Kagaku Kogyo Co., Ltd., its stated purity being 99.9 mol per cent. After repeated fractional distillation-condensation processes, the final purity was 99.998 mol per cent as determined from the fractional melting procedure.

The calorimeter assembly has been described in detail elsewhere(10). The temperature scale is based on a germanium and a platinum resistance thermometers calibrated on IPTS-68. No helium exchange gas was used inside the calorimeter.

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