DYNAMIC OF TRANSFORMATION UNDER THE HEAT TREATMENT OF A NEW CARBON PHASE CARBOLITE STUDIED BY CALORIMETRY

A.V. Palnichenko[a], A.F. Gurov[a], V.N. Kopylov[a], K. Kusano[b], S. Tanuma[b] and E.I.Salamatov[c]
[a]Institute of Solid State Physics, RAS, Moscow distr., 142432, Chernogolovka, Russia.
[b]Iwaki Meisei University, Chuodai, Iwaki, Fukushima 970, Japan.
[c]Physical and Technical Institute RAS, Izhevsk, 426001, Russia.

Introduction

Recently, a new carbon phase has been synthesized by quenching of high temperature carbon gas on a room temperature copper substrate. Due to the low value of the specific weight, 1.46 g/cm^3, the synthesized phase has been named carbolite [1].

Although the crystal structure of the phase is not known in detail, it is assumed consisting of quasi-one-dimensional carbon chains oriented along the *c*-axis of the hexagonal crystal lattice [1]. The inter-chain spaces yield a possibility of intercalation of the material by alkali metals and halogens [2]. By analogy with intercalated graphite and fullerene, the intercalation of carbolite may result in discovery of a new family of superconductors.

Experimental

The carbolite samples have been synthesized in an argon atmosphere by the method [1]. The material was in the form of flakes ranging in size from 1 mm^2 to 10 mm^2 and 3-10 μm in thickness.

The low temperature dependences of the specific heat *C(T)* have been measured by means of a home-made high sensitive relaxation microcalorimeter over the temperature range from 4.5 K to 30 K.

To assure good thermal contact for the specific heat measurements, the flakes were snugly compressed with each other by small pressure treatment. As a result the samples have taken the form of stacks of the flakes. The masses of the samples measured were 70 μg - 90 μg. The specific heat values for a fixed temperature, *T*, have been determined by averaging over a temperature interval equal to 1.5% of *T*. Addenda contribution to the total heat capacity was smaller than 30%.

For the measurements of *C(T)* dependences in the temperature range from 130 K to 730 K, a scanning Perkin-Elmer 7 calorimeter has been used. The calorimeter was operated by the heat power fed to the sample to ensure a constant heating rate equal to 20 K/min. The samples of the masses from 4 mg to 7 mg were chosen for these measurements.

Results and Discussion

The typical dependence of $C(T)/T^3$ on the temperature of carbolite sample is presented in Fig. 1.

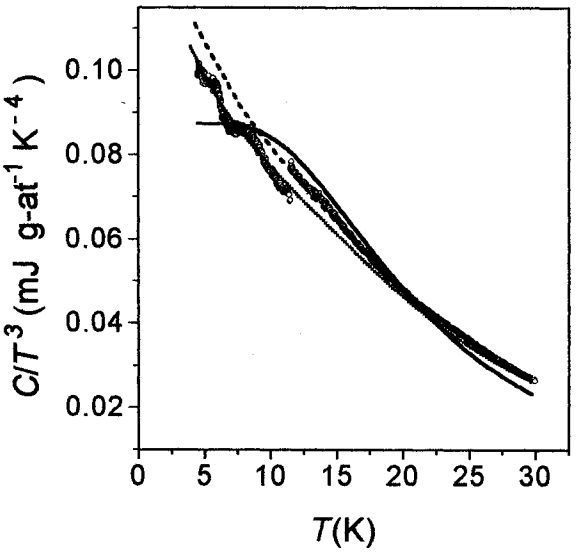

Figure 1. The dependences of the specific heat divided by temperature cubed, C/T^3, on the temperature *T* of the carbolite sample. The bold circles are the experimental data. The solid line is the best fit to the experimental *C(T)* dependence using a standard Debye model with Θ_D=100 K. The dashed and dotted lines correspond to the two independent fits to the experimental *C(T)* dependence at $T>11.5$ K and $T<11.5$ K using the model described in [3,4], respectively.

From Fig 1, a broad smooth anomaly of the *C(T)* dependence at 6-8 K and an abrupt step-like one at 11.5 K are clearly seen. The anomaly at 11.5 K is attributed to the effect of freezing of some vibration or rotation degrees of freedom of atoms or atomic complexes in carbolite at $T<11.5$ K.

The best fit to the experimental *C(T)* dependence, using a standard Debye model with Θ_D=100 K, is

unsuitable to describe the observed $C(T)$ dependence, Fig.1. For this reason, to explain the measured $C(T)$ dependence, a model for the heat capacity of the quasi-one-dimensional crystals has been used [3,4]. Within the frames of this model, the crystal is considered as a medium, consisting of the chain-molecules oriented along the z-axis. The molecules are weakly bounded to each other, in comparison with the intramolecular bounding, and are proposed to be the continuum. Since the experimental $C(T)$ dependence exhibits an abrupt anomaly at 11.5 K, the two independent fits to the $C(T)$ at T<11.5 K and T>11.5 K have been performed. The resulted fits are shown in Fig 1.

From the calculations, the values of $v_{T,z}$, and $v_{L,xy}$ have been estimated as $24 \cdot 10^3$ m/s, and $4 \cdot 10^3$ m/s at T<11.5 K, and $15 \cdot 10^3$ m/s, and $4 \cdot 10^3$ m/s at T>11.5 K, respectively, where $v_{T,z}$ and $v_{L,xy}$ are the transverse polarization sound velocity along the z-axis and the longitudinal polarization sound velocity in the xy-plane, respectively. The estimated value of $v_{L,xy}$ is reasonable in comparison with the known values for the wide range of different materials. However, the values of $v_{T,z}$ are comparable to that of diamond.

The high temperature dependences of the effective specific heat, C_{eff}, for carbolite sample are shown in Fig. 2. The value of C_{eff} is determined as the ratio of the heat flow value, fed to one gram-atom of carbolite, to the value of the sample heating rate, providing the constant heating rate in the $C_{eff}(T)$ measurements. In this measurements, the negative C_{eff} values correspond to the exothermic transformations in the sample upon heating.

The curves 1-3 correspond to the three consecutive $C_{eff}(T)$ scans over the same sample. In order to demonstrate the resolution of the measurements, the $C_{eff}(T)$ scan of the empty calorimeter is represented by curve 4. As seen from curve 1, in the first scan, the sample undergoes the exothermic process starting from T≈350 K, which is still not terminated at T=730 K. Against the background of the exothermic process, the relatively narrow anomaly is observed at T≈650 K. The consecutive scans, shown in curves 2 and 3, do not exhibit this anomaly but still contain the broad anomaly, remaining from the exothermic process, which is diminished from scan to scan.

On the basis of the high temperature specific heat and the X-ray powder diffraction measurements, it has been found that carbolite is a metastable phase under the normal conditions, which undergoes the irreversible complicated transformations at the temperatures above T≈350 K to the final amorphous state.

In this respect we should note that, on the one hand, the carbolite crystals grow only in the ambient high temperature carbon gas (T>>4000 K), while on the other hand, the material readily transforms to the amorphous state under the comparatively low temperature annealing. These important facts should be taken into account for successful carbolite synthesis.

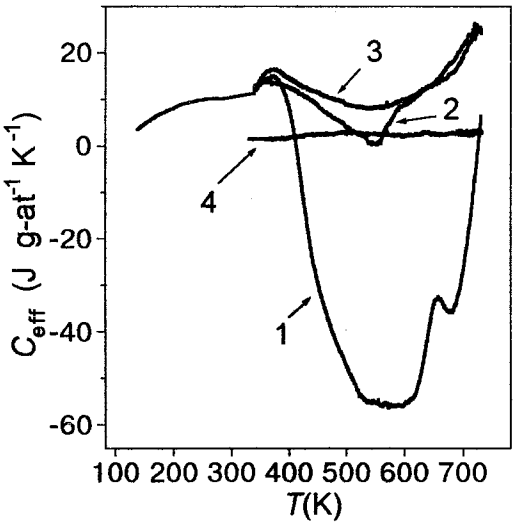

Fig.2. The high temperature dependences of the specific heat, $C_{eff}(T)$, of the carbolite sample.

Acknowledgments

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References

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