Thermal conductivity and thermopower of vapor-grown graphite fibers

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Values for the thermal conductivity and thermopower of graphite fibers grown by pyrolysis of natural gas are reported between 10 and 370 K. The measurements were made along the fiber axis on both as-grown fibers and fibers heat treated to 3000 °C. It is shown that heat treatment improves the thermal conductivity by a factor of 50: at room temperature highly heat-treated fibers rank among the very best thermal conductors available. We quantitatively interpret our low-temperature thermal conductivity data using the phonon dispersion relation for graphite. Remarkable agreement is achieved between the phonon mean free paths we deduce from our measurements and defect structures we identify in electron micrographs. The thermopower data we report on the highly heat-treated fibers are very similar to those obtained on single-crystal graphite.

INTRODUCTION

The thermal conductivity of high-quality graphites (see Ref. 1) is remarkably high: Room-temperature values up to 2000 $W m^{-1} K^{-1}$ have been reported on natural single crystals and highly oriented pyrolytic graphite (HOPG). Considerable progress has also been made in theoretical modeling of the temperature dependence of such materials.[1]

As early as 1957,[2] thermal conductivity values between 20 and 300 K have been reported for graphite filaments prepared by pyrolysis of methane. More recently, measurements on benzene-derived fibers[3] have confirmed that vapor-grown fibers, when heat treated to 3000 °C, share the heat conduction properties of HOPG and single crystals.

The aim of the present work is to report the first thermal conductivity data on fibers produced by the pyrolysis of natural gas, both *as-grown,* and when heat treated to 3000 °C. All measurements were made along the fiber axis. We illustrate the influence of heat treatment on thermal transport and correlate this to changes in structure. Similarly, Hooker and co-workers[4] studied the thermal conduction of pyrolytic graphite in relation to its defect structure. However, their samples were deposited at least at 2000 °C, while two samples studied in the present work have never been heated above 1130 °C.

From the low-temperature thermal conductivity data we deduce a value of the defect-limited phonon mean free path. A structural study in scanning electron microscope (SEM) reveals boundaries in the fiber heat treated at 3000 °C which are spaced at distances remarkably similar to the mean free path obtained. We also identify probable mean-free-path-limiting defects in as-grown fibers from lattice fringing images that were taken on a slightly different fibers.

The thermopower measurements we report closely resemble those reported on benzene-derived fibers,[5] thus confirming the similarity of the transport properties of the two types of fibers.

EXPERIMENT

The carbon fibers were grown by pyrolysis of natural gas,[6] and one batch of about 100 fibers was heat treated to 3000 °C. A summary of the characteristics of the fibers is given in Table I.

X-ray diffraction measurements were used to yield the interatomic spacings. We also deduce values of the x-ray coherence length along the c axis, L_c, from the $\langle 002 \rangle$ peak broadening using Scherrer's formula.[7,8] The electrical conductivity of a few individual fibers from each batch was measured at room temperature, using a dc four-probe method and an optical microscope to determine the geometrical parameters.[8]

The thermal conductivity and thermopower measurement apparatus is based on a closed-cycle refrigerator. To the cold plate of the refrigerator, a temperature-controlled copper block of 2 cm height is attached which dampens the thermal oscillations of the refrigerator. The measurement system (see Fig. 1), attached to this copper block, is based on the classical heater and sink method.[9] A rigid but thin (0.1 mm) fiberglass-epoxy frame holds the heater, the thermometry (a differential Chromel-Constantan thermocouple) and the current and voltage probes (Chromel wires). The heat losses of the system were calibrated by operating it without a sample. Below 100 K, the heat losses are essentially due to the conductance of the fiberglass-epoxy frame and wires, typically 3×10^{-5} $W K^{-1}$ at 12 K. Above 150 K, the heat losses follow a T^3 law characteristic of radiative heat loss, with a value at 298 K of 1.2×10^{-3} $W K^{-1}$, a rather low number obtained with the aid of multiple radiation shields.

The absolute thermopower of our chromel voltage probes was calibrated by mounting a 0.25-mm-diam lead wire (Johnson & Matthey Puratronic, 99.9985% purity), and measuring its thermopower versus our Chromel wires. The values of absolute thermopower for lead[10] were then subtracted, and the thermopower of our Chromel wires obtained. The accuracy of the procedure is estimated to be ±0.1 $\mu V K^{-1}$. From each batch of fibers, individual

TABLE I. Summary of the structural properties of the samples studied: the maximum temperature they were heated to (row 1), the lattice spacings corresponding to the ⟨002⟩, ⟨004⟩, ⟨100⟩, and ⟨101⟩ x-ray diffraction peaks, the correlation length L_c along the c axis, and the room-temperature values of the electrical resistivity ρ(RT). Parameters a and b are results from fits of Eq. (1) to the low-temperature experimental thermal conductivity data. L_ϕ is the in-plane phonon mean free path.

	Units	Sample 1	2	3
Maximum temperature	°C	1130	3000	1130
$d\langle 002\rangle$	nm	0.347	0.335	0.349
$d\langle 004\rangle$	nm	0.171	0.168	
L_c	nm	4.0	48.0	2.0
$d\langle 100\rangle$	nm		0.213	
$d\langle 101\rangle$	nm		0.203	
ρ(RT)	Ω m	1.02×10^{-5}	7.15×10^{-7}	1.24×10^{-5}
a		1.35×10^{-4}	0.152	
b		2.30	2.17	
L_ϕ	nm	3.6	2900	

filaments of diameters ranging between 20 and 50 μm were chosen, and glued with silver paint to the ends of the fiberglass-epoxy frame. The sample voltage probes were attached with flexible silver paint. For the fibers heat-treated to 3000 °C (sample 2 in Table I) we used 12 filaments. In the case of the as-prepared fibers, sample 1 in Table I, 57 filaments were used. The results for the thermal conductivity are reported only if the total thermal conductance was more than 1.4 times that due to heat losses. Thus, for example, sample 3 in Table I consisted of only 10 filaments and the above thermal-conductance criterion was not satisfied; therefore only thermopower values were reliably obtained.

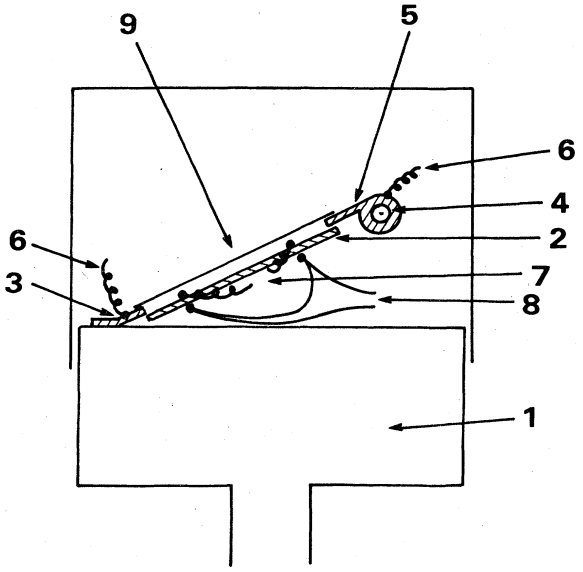

FIG. 1. Experimental setup. A closed-cycle refrigerator cools a temperature-controlled heat sink (1), to which a rigid fiberglass-epoxy frame (2) is attached by means of a copper clamp (3). The other end supports a heating element (4) embedded in another copper clamp (5). Two Constantan wires (6) can feed current through the sample. Two Chromel wires (7) measure the voltage and a differential thermocouple (8) the temperature gradient across a sample (9) that is glued to heater (5), sink (3), and voltage probes (7) with flexible silver paint.

Piraux *et al.*[3] made careful thermal-conductivity measurements on both single fibers and bundles of fibers, and found no significant discrepancy between the two methods. For this reason, we assume that the results we report for the thermal conductivity on bundles of several fibers is an average value weighted by the cross-sectional area valid for the individual filaments. The thermopower presumably also is an average, but weighted by the individual electrical conductances of the fibers.

RESULTS AND DISCUSSION

In Fig. 2, we report values for the temperature dependence of the thermopower of the present fibers. The data shown for the as-grown fibers were obtained on samples of two different batches. As already pointed out the results are similar to those obtained on benzene-derived fibers.[5] However, on the fiber heat treated to 3000 °C, we do not observe a region of positive Seebeck coefficient, as Endo *et al.*[5] do between 60 and 200 K. In a nearly compensated semimetal, which the highly heat-treated fibers are, the thermopower is very sensitive to the asymmetry between the carrier properties: minute differences between densities and mobilities of electrons and holes. It is therefore not surprising that a considerable scatter is observed in the thermopower of "very perfect" pyrographites,[1,11] and hence this probably also is the case in vapor-grown fibers.

A log-log plot of the temperature dependence of the thermal conductivity for the as-prepared and 3000 °C heat-treated fibers is shown in Fig. 3. The thermal conductivity of the 3000 °C heat-treated sample (upper curve) has a maximum in the vicinity of $\sim$160 K and a $T^{2.3}$ behavior for $T < \sim$40 K. This behavior is very similar to that observed for heat-treated benzene-derived fibers,[3] HOPG,[12] or even natural single-crystal graphite.[13] The thermal conductivity of the as-prepared fibers, Fig. 2 (lower curve) is smaller by about a factor of 50 at 300 K. The peak in the thermal conductivity is shifted to higher temperature beyond our measurement capabilities. In our whole measurement range, the thermal conductivity is due

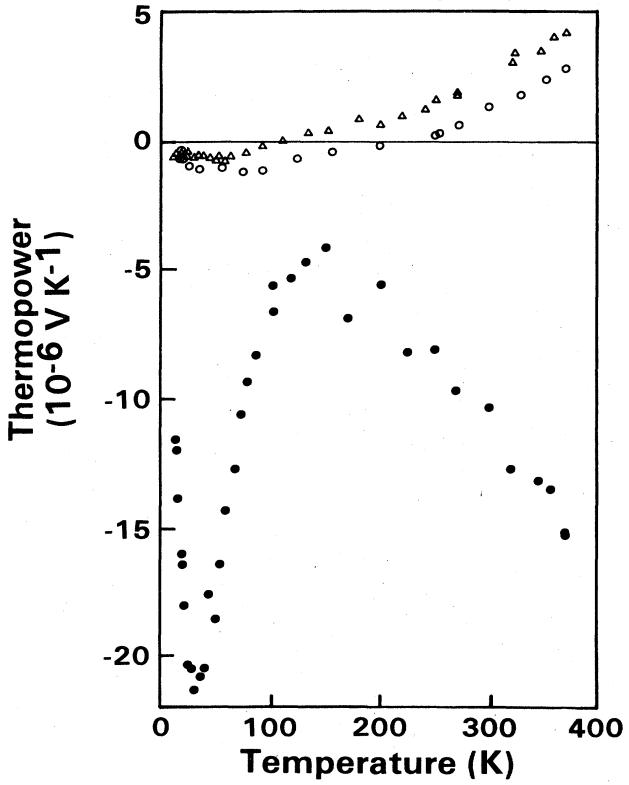

FIG. 2. Thermoelectric power of vapor-grown graphite fibers as a function of temperature. The sample heat treated at 3000 °C yields the lower curve, the two not-heat-treated ones (sample 1, △; sample 3, ○) have a similar behavior.

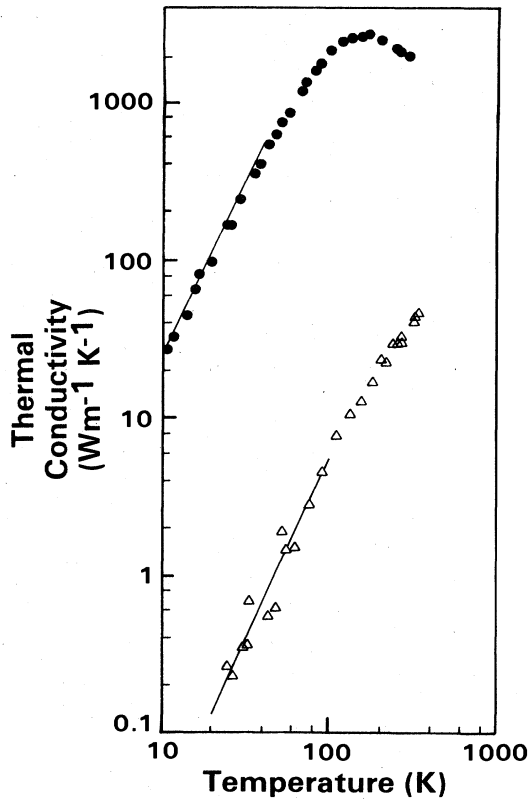

FIG. 3. Temperature dependence of the thermal conductivity of vapor-grown fibers, sample 1 in Table I, not heat treated (lower points), and sample 2, heat treated to 3000 °C (upper points). The lines represent the calculated low-temperature basal-plane thermal conductivity of graphite, assuming $C_{44}=0$ and $L_\phi=3.6\times10^{-9}$ m (lower line) or $L_\phi=2.9\times10^{-6}$ m (upper line).

to heat transported by lattice waves. The electronic contribution can indeed be estimated using the Wiedemann-Franz law (see Ref. 9) with the measured electrical resistivity[8] of our samples, and is found to be negligible. The theory of the lattice thermal conductivity of graphite, when limited by phonon scattering on defects or grain boundaries, has been developed by Kelly[14] and is conveniently summarized in Ref. 1. In essence the theory calculates the total heat conducted, which is the sum of the contributions of all phonon modes that have a propagation vector lying in the plane. This is the only direction we need to consider due to the high degree of preferred orientation of the graphite-layer planes along the fiber axis.[5,6,15] The three essential modes are those with longitudinal in-plane, transverse in-plane, and transverse out-of-plane vibration direction. For each mode, the contributions of all possible momenta are integrated over the Brillouin zone. The simple case we shall further consider is that where the phonon mean free path L_ϕ is independent of temperature, momentum, and mode, because it then becomes a scaling factor in front of the integrals over the Brillouin zone. We assume this is to be the case at low temperatures (<50 K for the heat-treated fibers, and <100 K for the as-prepared fibers), where the phonons are dominantly scattered on defects, the nature of which is the subject of the next section. In such circumstances, a three-dimensional isotropic solid a exhibits T^3 dependence of thermal conductivity and a two-dimensional solid a T^2 dependence. In graphite, where the out-of-plane vibrating phonons have a lower Debye temperature and group velocity than the other modes,[1] it is not surprising to observe an intermediate power law in the low-temperature range:

$$K=aT^b\ . \tag{1}$$

The values of constants a and b for our samples have been fitted to the data in Fig. 2 and summarized in Table I. If we follow the calculations of Kelly[14] with the elastic constant $C_{44}=0$, and the other elastic constants assuming the value they have for pure graphite,[1,14] a low-temperature power law $b=2.28$ is theoretically expected and in good agreement with our data. Therefore, if we use Kelly's model[14] to fit our data quantitatively, we obtain a value for the phonon mean free path L_ϕ, which is reported in Table I for each sample. The solid lines in Fig. 3 represent the thermal conductivity so calculated. As stated previously, we believe the mechanism limiting the value of L_ϕ is scattering of phonons by defects, and shall further elucidate their nature.

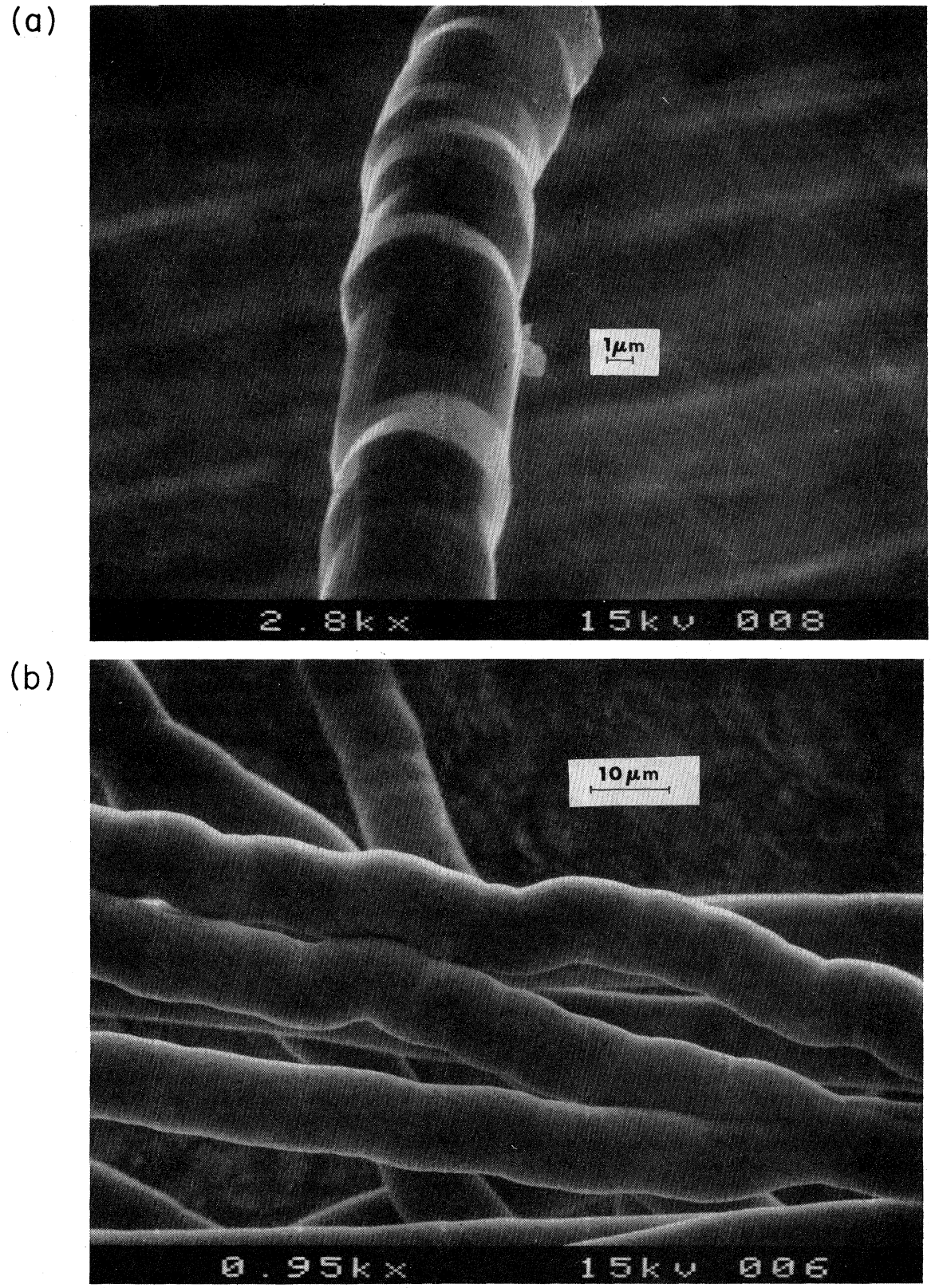

FIG. 4. Micrographs illustrating the faceting along the length of vapor-grown fibers. (a) A fiber heat treated at 3000 °C shows alternating dark and light areas along its length, facets. (b) A similar fiber, but before heat treatment, shows a smoothly undulating surface. We believe the undulations become facets during heat-treatment. (c) A fiber which appeared smooth on the surface, but after fracture exhibits a similar undulation in its interior structure.

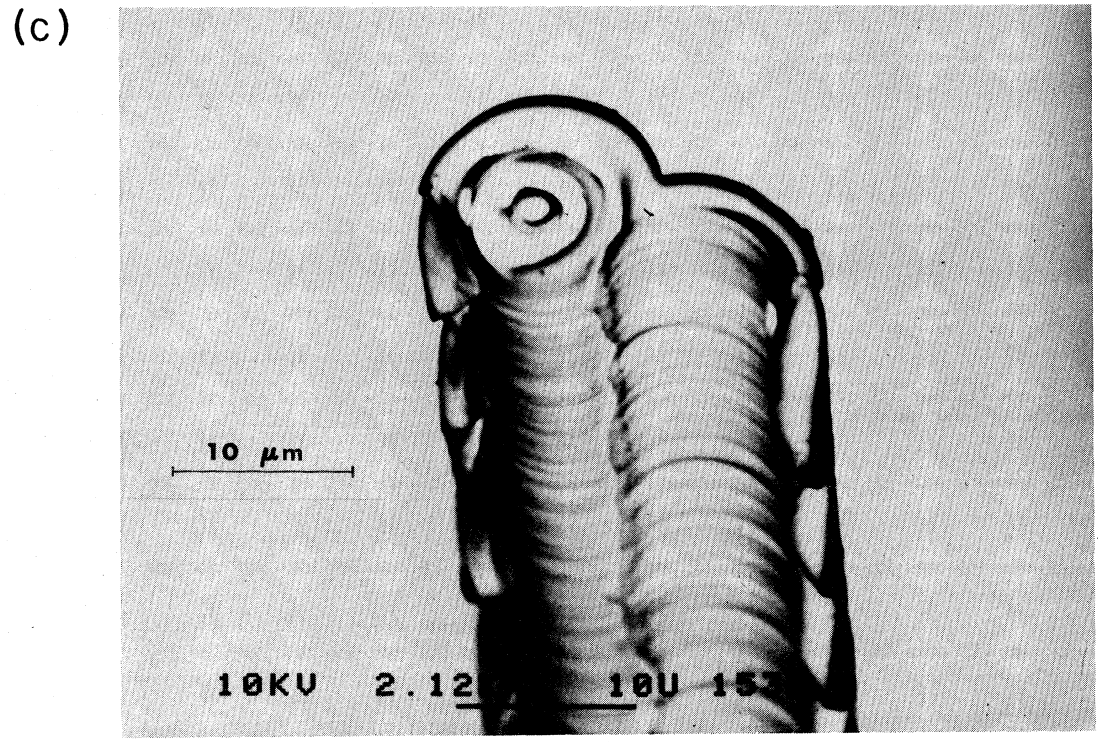

FIG. 4. (*Continued*).

OBSERVATIONS OF MICROSTRUCTURAL DEFECTS

The 3000 °C heat-treated samples used for the thermal conductivity measurements were observed in a simple scanning electron microscope (ISI-SX30). Close inspection of the fibers revealed immediately that many exhibited well-defined faceted surface features seen for example in Fig. 4(a). This phenomenon has also been previously observed for heat-treated benzene derived fibers.[16] Analysis of a sample of 32 such facets on five different fibers yields an average facet size $\sim 2.8\times 10^{-6}$ m with the range of sizes from $\sim 1\times 10^{-6}$ m to $\sim 8\times 10^{-6}$ m. The average size of the faceted surfaces on the fibers is in good agreement with the L_ϕ values obtained from the thermal-conductivity data. This would imply that the defects scattering the phonons are the boundaries of the faceted areas. The facets have their origins in an undulating surface structure that is present on the as-prepared fibers (see Fig. 4). The undulating surface on the as-prepared fibers is a result of the so called "thickening" step[17] during the fiber-growth process in which tiny precursor fibers $\sim$200—500 nm are thickened by carbon chemical-vapor deposition (CVD).

Several of the fibers in our sample exhibited smooth uniform surfaces rather than the faceted surface structure. We also found smooth fibers among the as-prepared fibers. Fracture of such samples revealed that the core of the smooth fiber indeed exhibited the undulating microstructure [Fig. 4(c)] which was covered by a smooth carbon surface. It is well known that the density of CVD deposited carbons can have a range of values dependent on the spatial location in the CVD reactor.[18] It is reasonable to assume that the smooth fibers were located in a different part of the fiber growth tube than those which exhibited the undulating surface. The exact cause of the smooth surface which does not facet with high-temperature heat treatment is not known but is most probably due to process-induced transients in the carbon concentration in the reactor. Nevertheless the strong correlation between the thermal mean free path and the average facet size identifies the facet boundaries as the most probable defect for phonon scattering.

Pictures of ⟨002⟩ lattice fringes on parts of an as-grown fiber deposited from benzene have been published.[19] While the "precursor" filaments show a rather perfect lattice, most of the material the fibers consist of is pyrolytically deposited graphite, of which a picture is available in Ref. 19. The average length of the individual graphite layers in this picture is remarkably close to the phonon mean free path we report, $\sim 3.6\times 10^{-9}$ m.

CONCLUSIONS

This paper reports the first thermal-conductivity data on not heat-treated vapor-grown fibers. It interprets the thermal conductivity of these fibers both as-grown and heat treated to 3000 °C, in the temperature regime where phonon-defect scattering dominates heat transport. And it finally illustrates how microscopy and thermal conduc-

tivity complement each other in characterizing the defect structures of materials: the value of the phonon mean free path does not in any way contain as much information on the morphology as a micrograph does, but it is an average property of the whole sample.

ACKNOWLEDGMENTS

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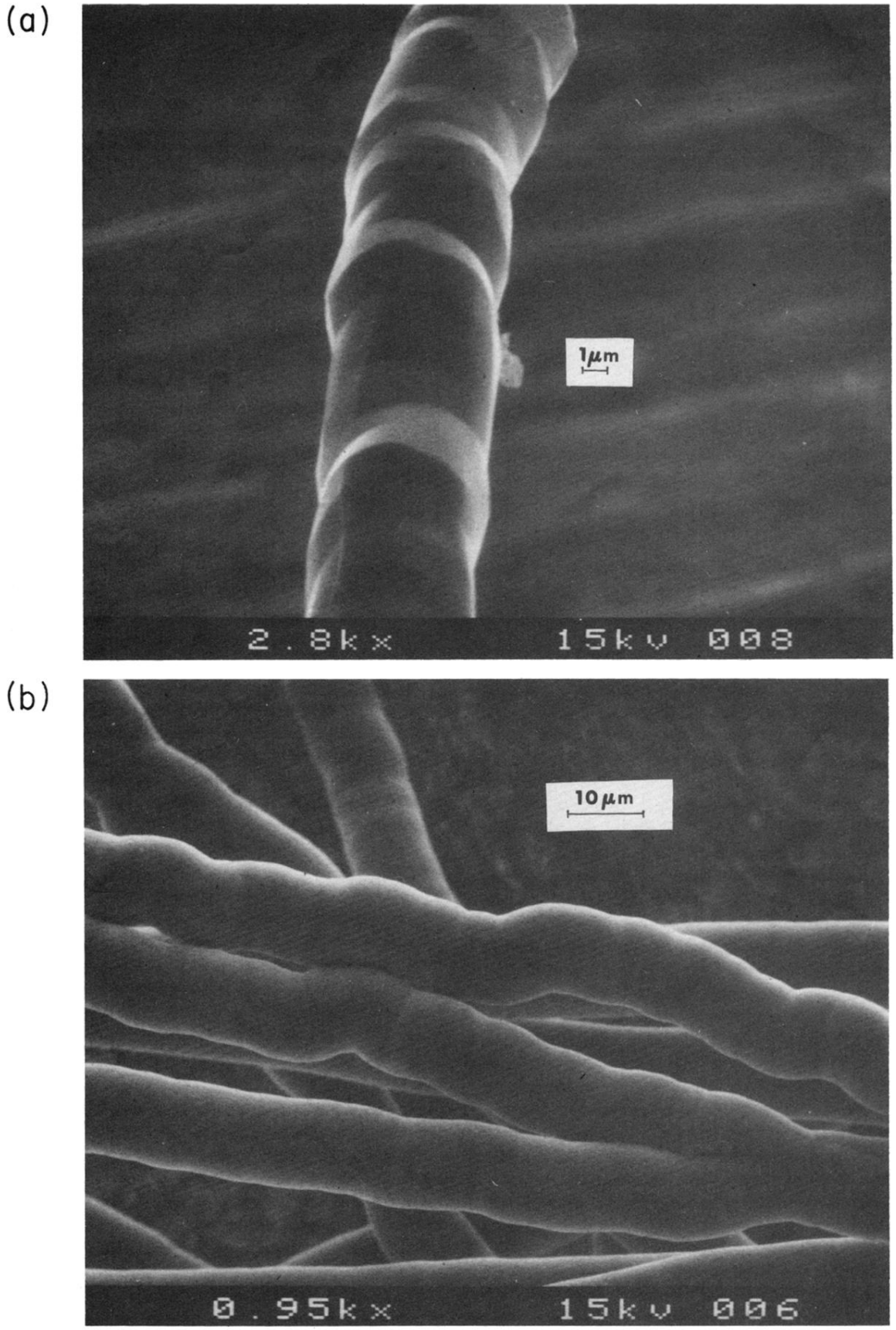

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(c)

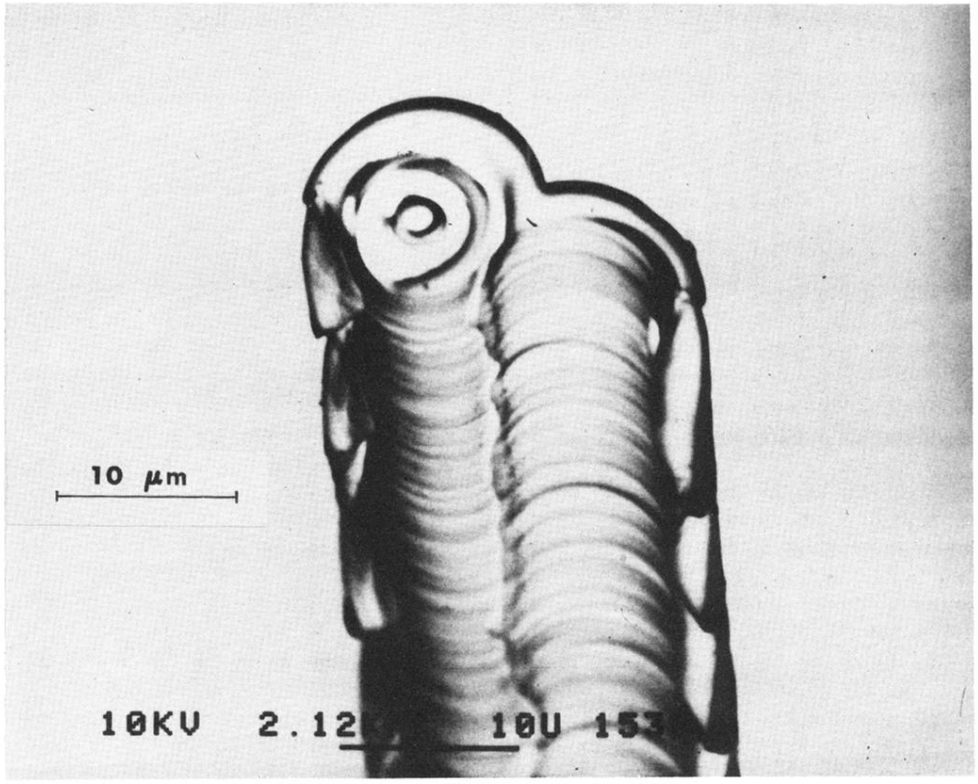

FIG. 4. (*Continued*).