MASTER

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TEMPERATURE DEPENDENCE OF PHONONS IN PYROLITIC GRAPHITE

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Dispersion curves for longitudinal and transverse phonons propagating along and near the c-axis in pyrolitic graphite at temperatures between 4°K and 1500°C have been measured by neutron spectroscopy. The observed frequencies decrease markedly with increasing temperature (except for the transverse optical "rippling" modes in the hexagonal planes). The neutron groups show interesting asymmetrical broadening ascribed to interference between one phonon and many phonon processes.

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Dispersion curves for longitudinal and transverse phonons propagating along[1,2] or near[2] the c-axis in pyrolitic graphite at temperature in the range 4°K to 1500°C have been measured using a triple-axis neutron spectrometer[3]. The specimens (Union Carbide Co.) had a mosaic width of 0.8°. The results are presented in Figs. 1-6, with captions.

The Roman numerals in Fig. 1 indicate the configurations used in different types of "Constant $\vec{Q}$" experiments:

I - Frequencies for LA and LO modes along the c-direction are determined from neutron groups in the usual way (Figs. 4 and 5).

II The cut off in the continuous energy distribution of scattered neutrons corresponding to the minimum wave vector $\vec{q}$, gives the frequencies of TA and TO modes along the c-axis (Fig. 6).

III - Because of their near-isotropy[2] in $\vec{q}$-space normal to the c-axis, acoustic "rippling modes" ($TA_{\perp}$) can be studied and their average frequencies determined in the usual way (Fig. 3).

IV - Similarly, optical "rippling modes" ($TO_{\perp}$) can be studied by reason of their near-isotropy (Fig. 3).

The experiments were not carried out in good geometry, nor were the intensities corrected for instrument efficiencies, so too-exact comparison with theoretical calculations is depreciated, and none has been made. The shifts and widths are well-determined, however.

The results are summarized as follows. The energy of the longitudinal zone boundary phonon at $|q| = 1/c$ varies with temperature as $1/c^{3.2}$, from 16.06 mev at 4°K to 13.77 mev at 1490°C. This agrees with results of Roy[4] over his more limited temperature range. The transverse modes show roughly the same behaviour, decreasing from 5.2 mev at 23°C to 4.6 mev at 1190°C. The dispersion curves for both longitudinal and transverse modes are closely sinusoidal in q at all temperatures; this fact indicates that appreciable interatomic forces exist only between first neighbour planes. At high temperatures the longitudinal modes on the linear part of the c-axis dispersion curve show a marked asymmetrical broadening which depends on the R.L. point and on whether q is + ve or - ve. (For the mode at $|q| = 0.3/c$ the F.W.H.M. is $\sim$0.6 mev or ~10% of the frequency.) The zone boundary longitudinal mode and the transverse modes show little broadening. These facts are understandable from considerations of conservation of energy and wave vector in three-phonon processes, and of interference[5-7] between the one-phonon and many-phonon components in the scattered neutron spectra. The rippling modes both show considerable broadening, but the $TA_\perp$ and $TO_\perp$ modes behave very differently as to their temperature shifts. This is understandable from the very large coefficient of thermal expansion for the c-axis ($\alpha_\parallel = 30\times10^{-6}$), and very small ones for the a-axis ($|\alpha_\perp| < 10^{-6}$): the $TO_\perp$ mode involves relative motion of the hexagonal planes while the $TA_\perp$ involves only rippling of the planes.

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Figure Captions

Fig. 1 - The reciprocal space diagram for pyrolitic graphite[1,2]. Away from the c-axis the R.L. points become rings, e.g. (100) by reason of the stacking disorder of the planes. The (large) zone boundary is located at (001), (003) etc.

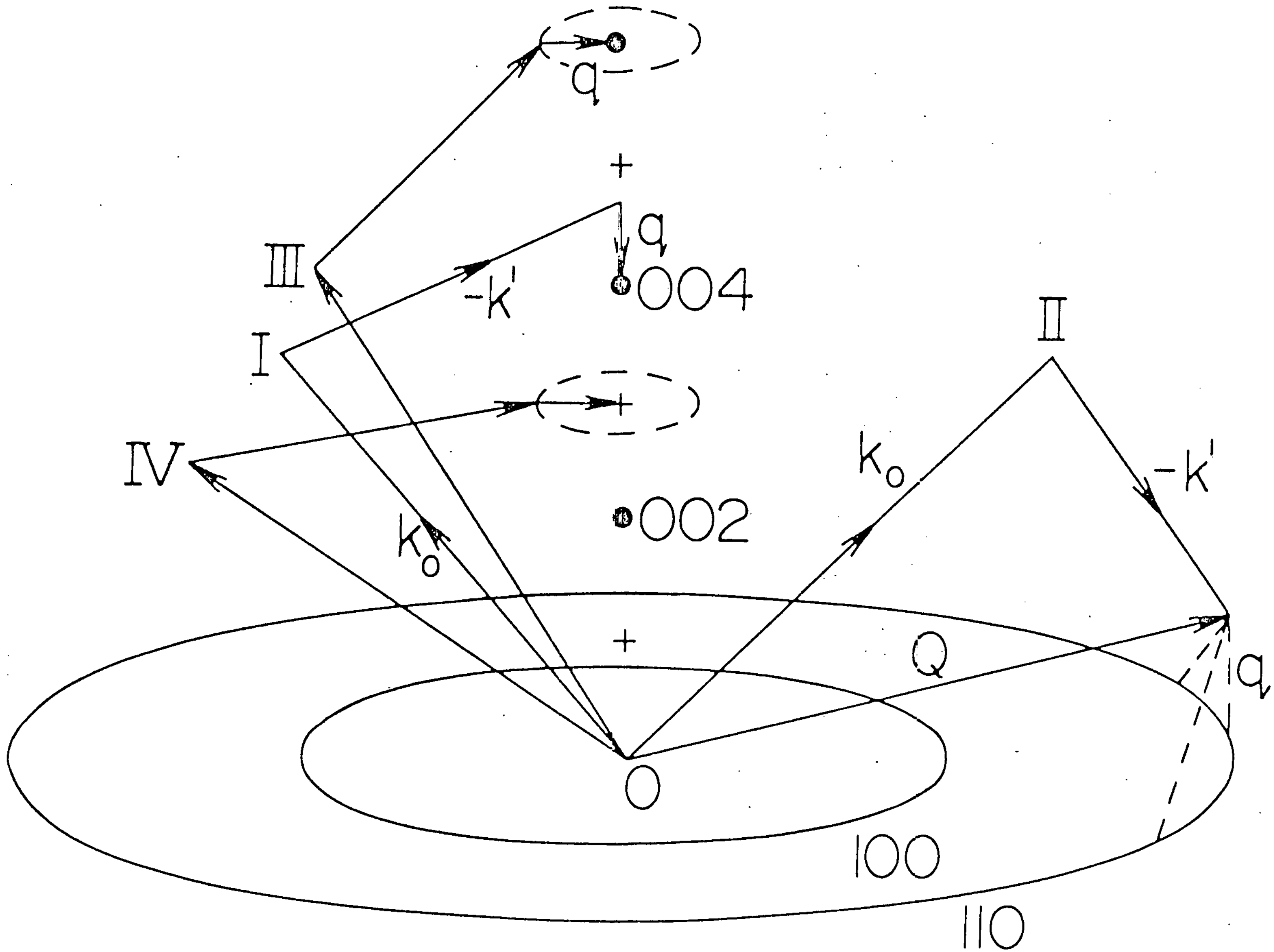
Fig. 2 - Dispersion curves along the symmetry directions in graphite at room temperature, as calculated from a model which fits neutron spectroscopy results by[2] Nicklow et al. The lower figure shows the part of the curves investigated in the present study. The two curves for the "rippling modes", $TA_\perp$ and $TO_\perp$, show the degree of anisotropy in the $\vec{q}$ plane. The LA and LO branches along the c-direction are continuous across the small (Brillouin) zone boundary, as are also the TA and TO branches. At 1200°C the dispersion curves are much the same but systematically lowered in frequency by about 12%, except for the $TA_\perp$ "rippling" branch which, if anything, increases in frequency - see Fig. 3.

Fig. 3 - Neutron groups for the $TA_\perp$ (top) and $TO_\perp$ rippling modes, measured for $\vec{q} = [|q_\perp|, q_c] = (4\pi/\sqrt{3}a)[0.15, 0]$ at room temperature and at 1200°C. Considerable broadening of the neutron groups over the resolution widths is evident in both cases. The shift in the $TO_\perp$ mode is very similar to that of the c-axis modes; in contrast, the average frequency of the $TA_\perp$ mode increases.

Fig. 4 - Neutron groups for the longitudinal (LA) mode on the near-linear part of the dispersion curve at $\vec{q} = (2\pi/c)[0,0,0.4]$, and for the LO mode at the Brillouin zone centre or, equivalently, at the large zone boundary $\vec{q} = (2\pi/c)(0,0,1)$ - (bottom). The LA modes on the linear part of the dispersion curve are much broader than are those at the zone boundary, and are asymmetrically shaped. The horizontal bars indicate calculated resolution widths (at half maximum), as in other figures.

Fig. 5 - Neutron groups for the mode L(0,0,0.3), taken at two different equivalent Q-points. The asymmetrical broadening is much more marked for $\vec{q} = (2\pi/c)(0,0,+0.3)$ than for $\vec{q} = (2\pi/c)(0,0,-0.3)$. A pattern taken at (0,3.7) was similar to that at (0,5.7).

Fig. 6 - Three experiments of Type II showing the cut-off of the intensity distributions which correspond approximately to the frequencies of transverse c-axis modes at the Brillouin zone boundary and the Brillouin zone centre. The horizontal bars indicate calculated resolution widths (FWHM) for neutron groups at these positions.



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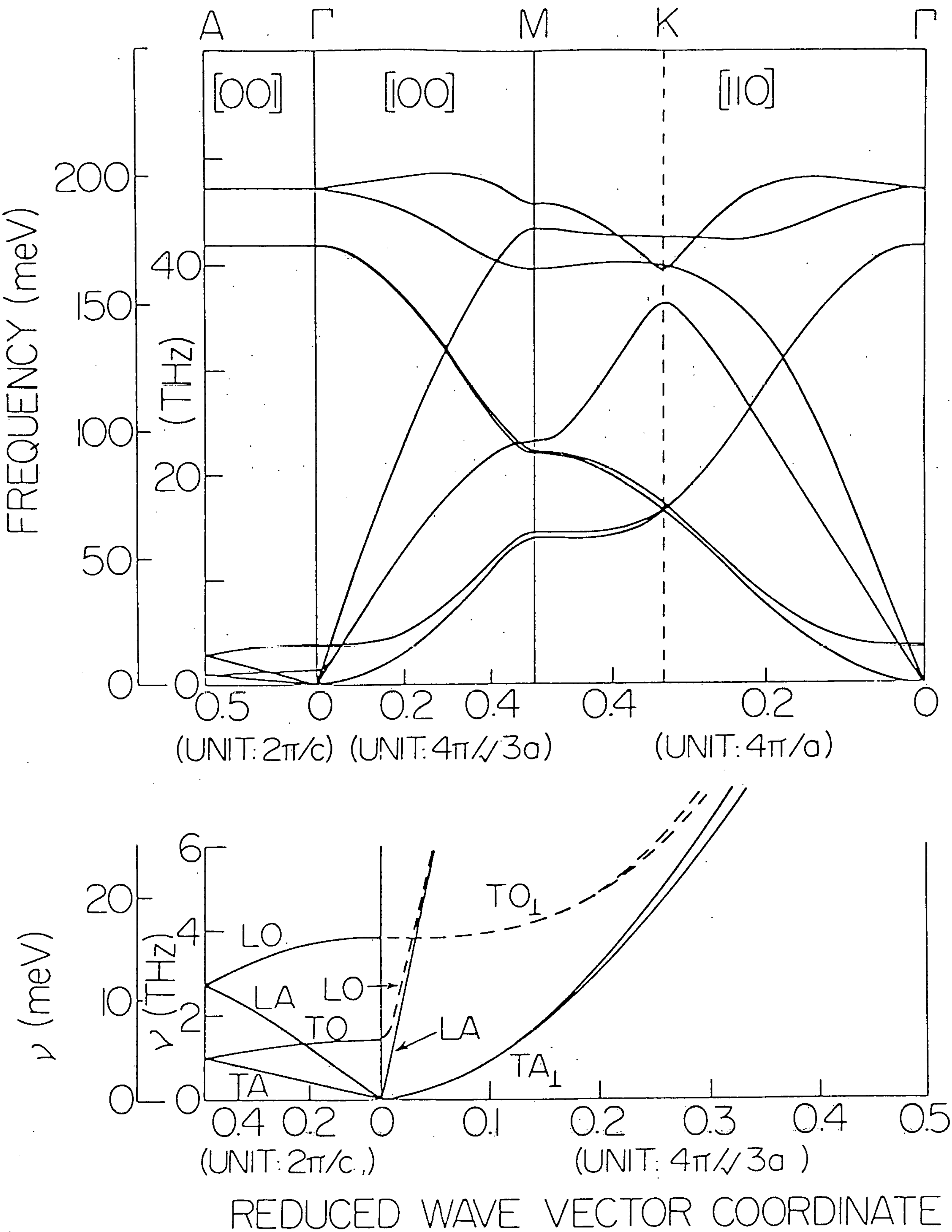
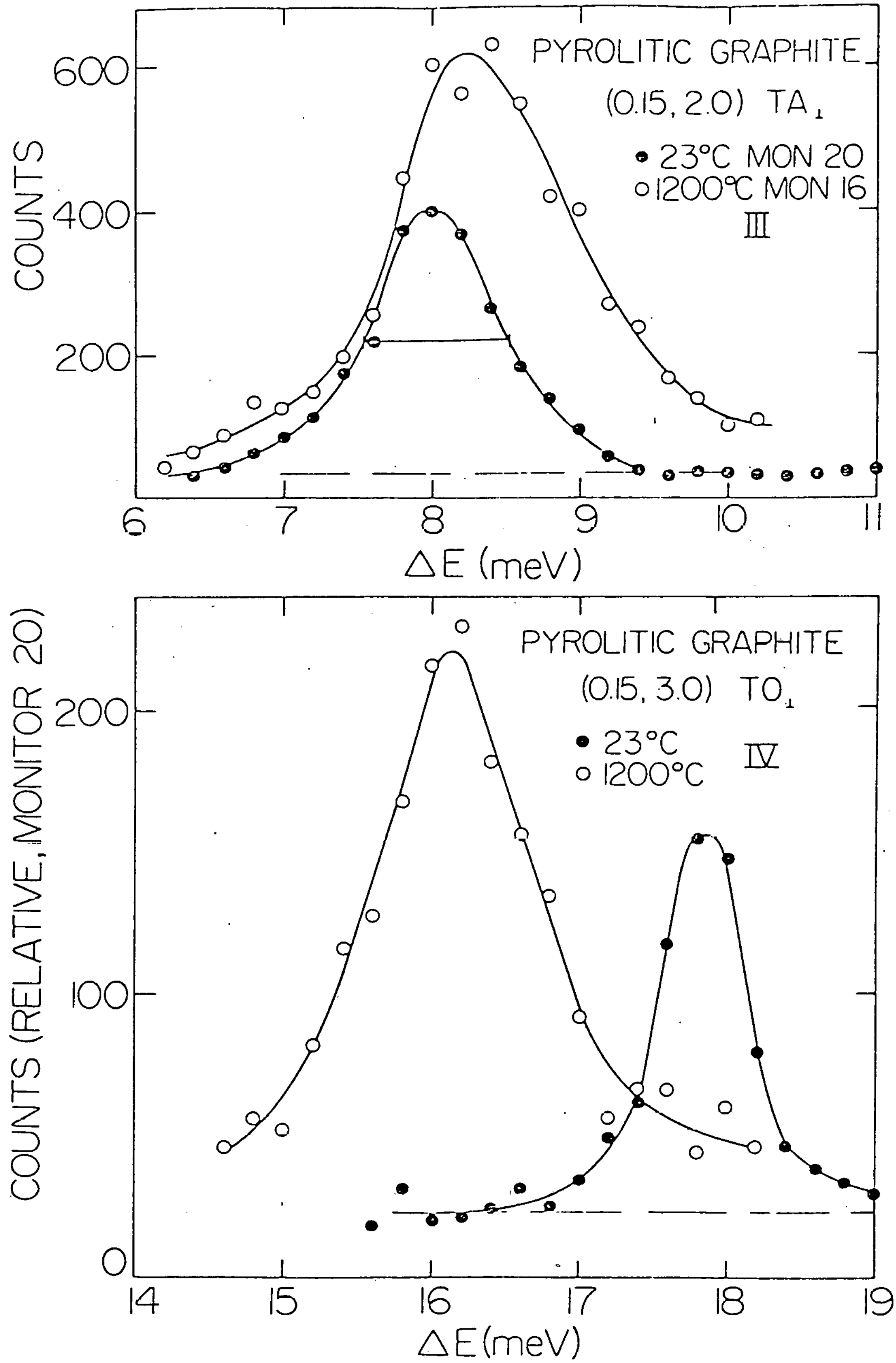


Fig 2 — BROCKHOUSE & SHIRANE



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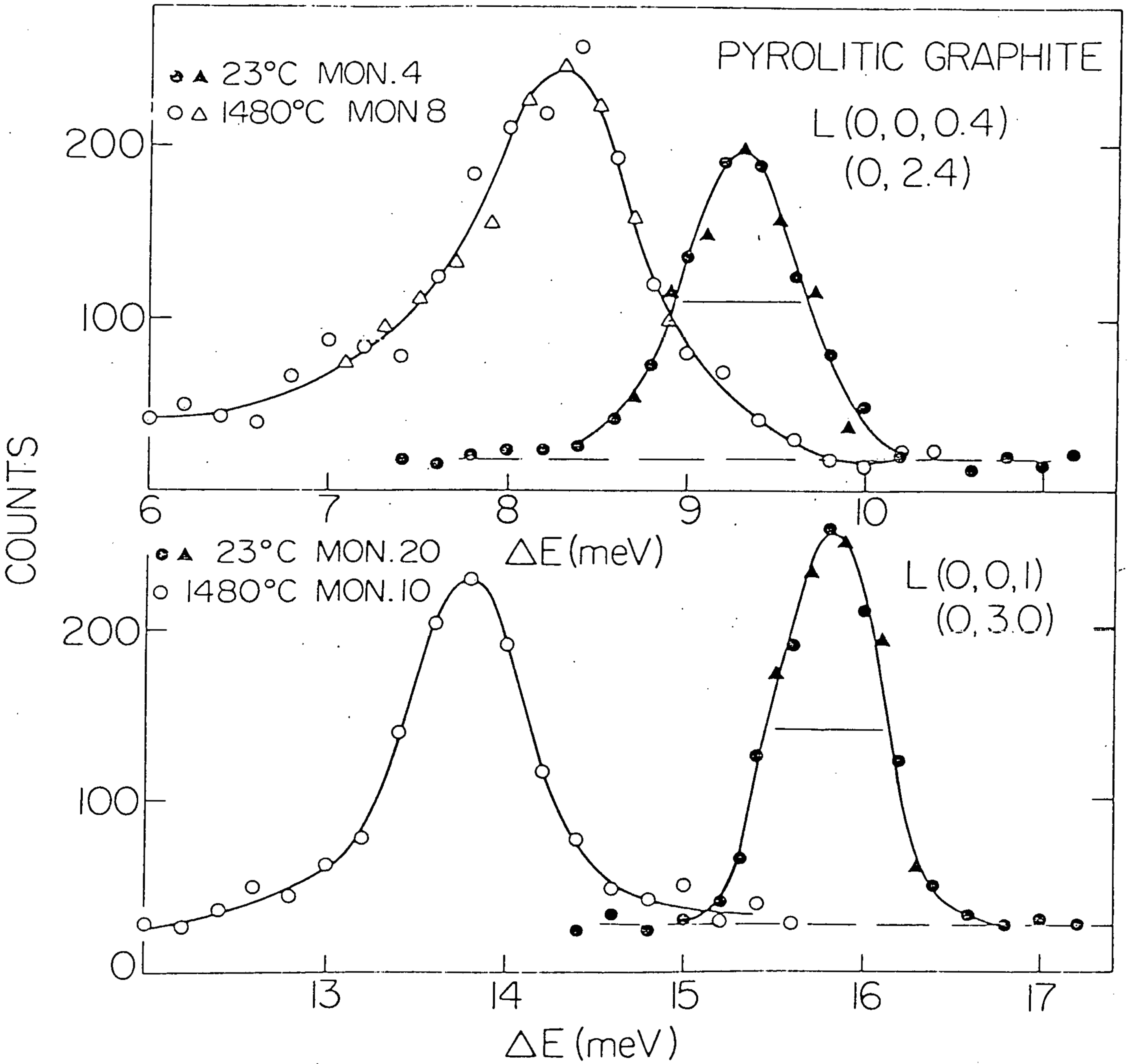

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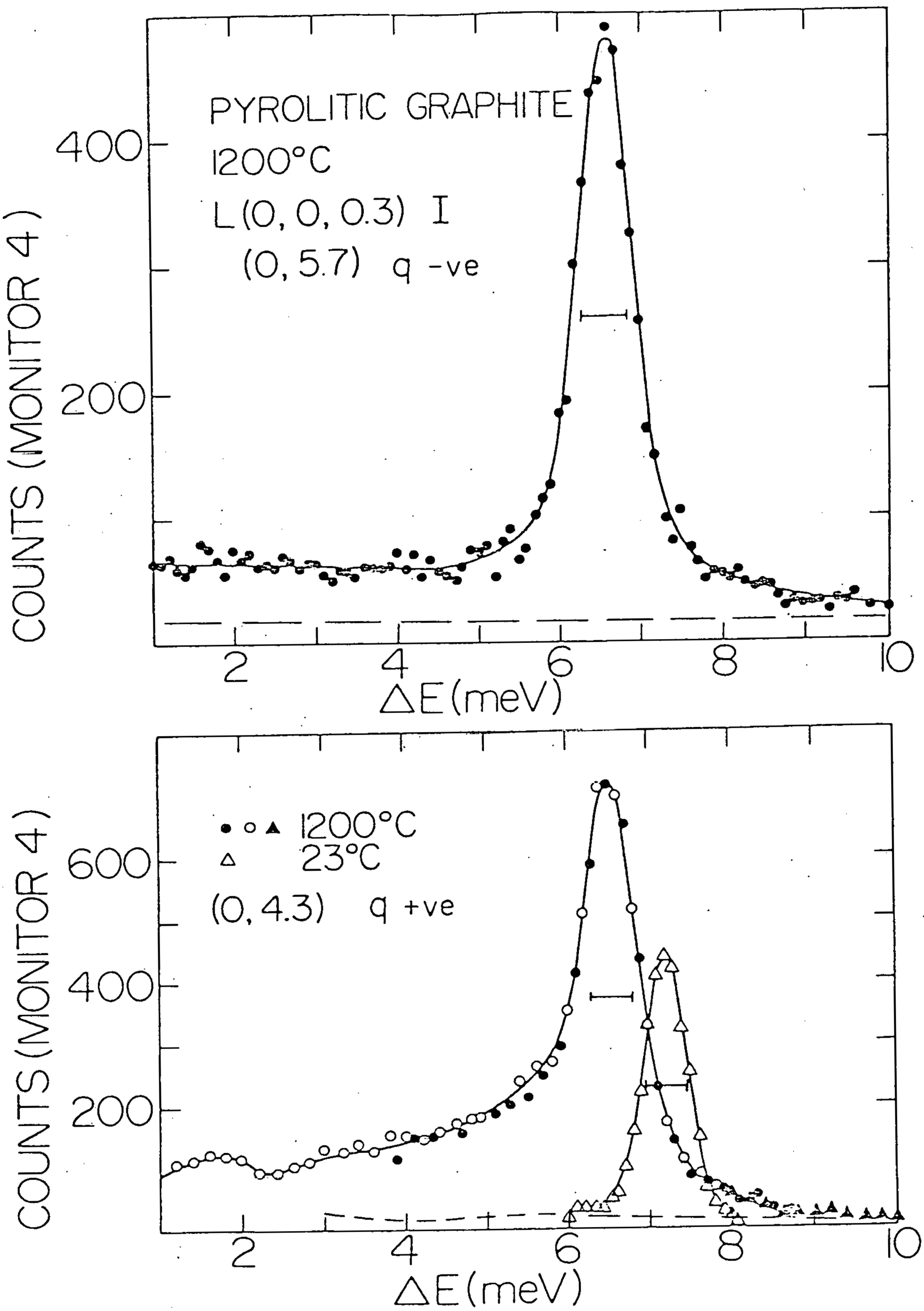

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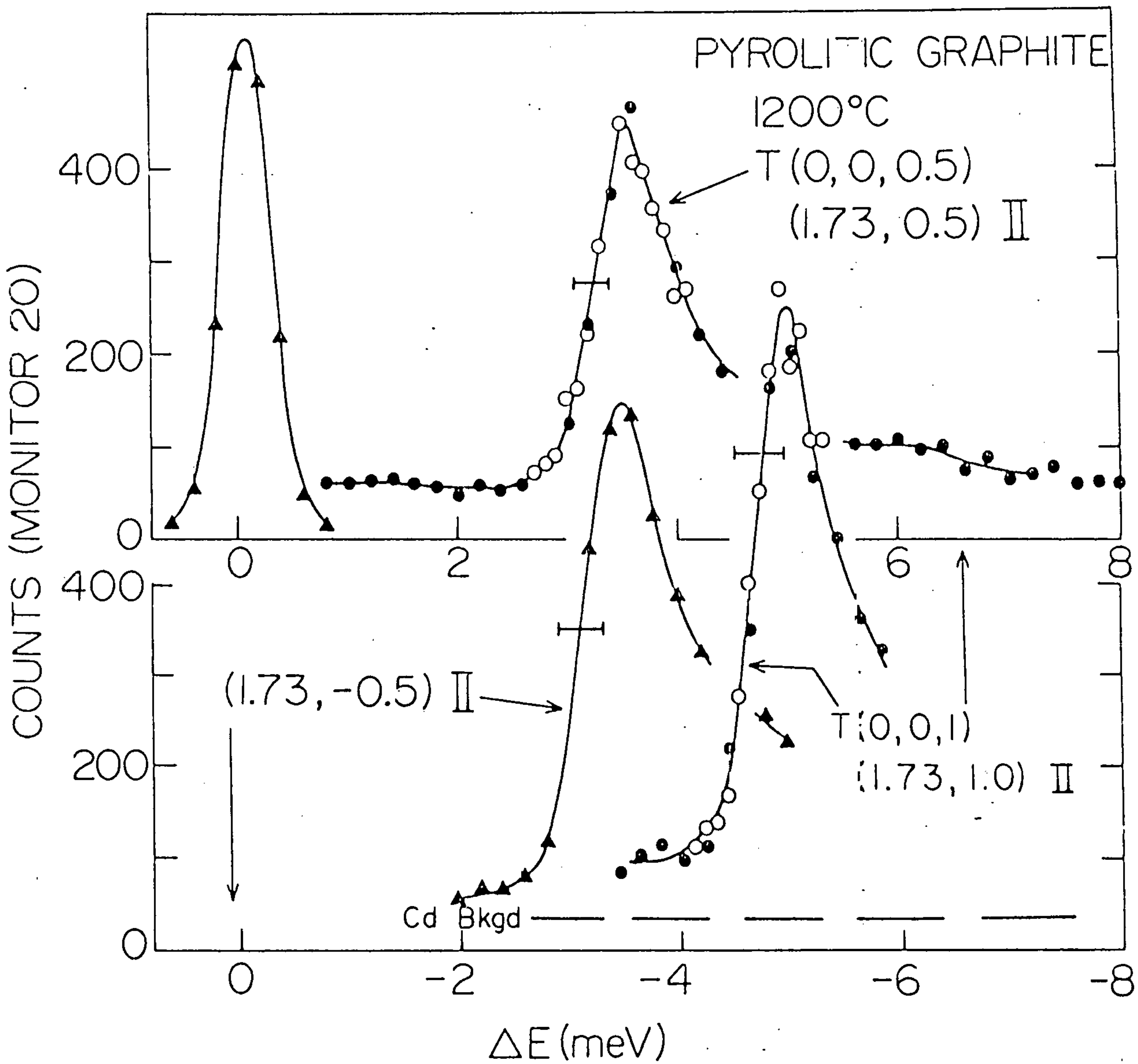

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