Letters to the Editor

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Communications

Polyethylene Frequency Spectrum from "Warm"-Neutron Scattering*

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SCATTERING data on highly crystalline polyethylene at 298° and 100°K have been reported by Danner *et al.*,[1] using the Brookhaven "cold-neutron" spectrometer. According to the model of infinite, uncoupled, extended carbon chains,[2] the only vibrational modes below the lowest optical limit at 720 cm^{-1} are two acoustic modes with frequency limits near 500–540 cm^{-1} (stretch–bend) and 190 cm^{-1} (C–C–C torsion). These modes are supposedly unobservable by infrared techniques[3] but should be recognized in neutron scattering by peaks at the frequency limits. Danner's 298°K data do show a strong peak near 190 cm^{-1} and a weak rise near 500 cm^{-1}. The 100°K data again show the 190-cm^{-1} peak, but the 500-cm^{-1} peak appears shifted to 570 cm^{-1} and is surprisingly increased in amplitude. As pointed out by the authors, this latter effect may have been due to limiting statistics. Also it is clear that the simple model is inadequate because additional structure appears: a strong peak at 140 cm^{-1}, a weak peak near 65 cm^{-1}, and a broad rise at 330 cm^{-1}.

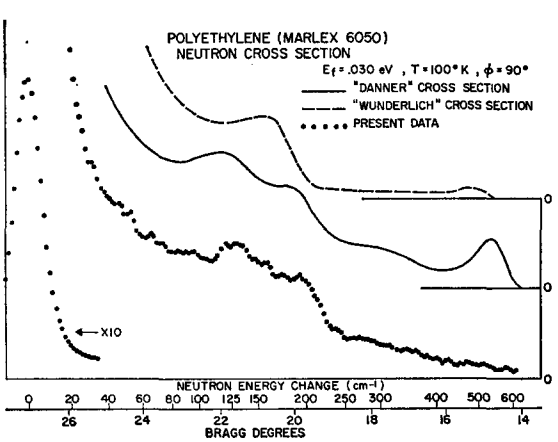

FIG. 1. Polyethylene (Marlex 6050) neutron cross section.

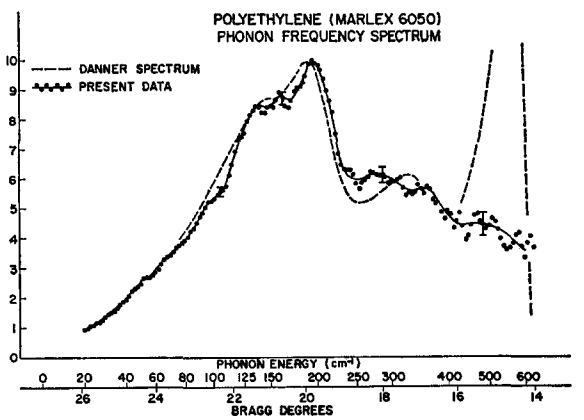

FIG. 2. Polyethylene (Marlex 6050) phonon frequency spectrum.

We report neutron data using a different scattering technique, but otherwise closely reproducing the "cold"-neutron experiment, i.e., the same target material,[4] 0.029 in. thick, 89.7% crystalline Marlex 6050 at 100°K, and a 90° scattering angle. Neutrons are downscattered from variable "warm" energies to a fixed final energy of 0.030 eV in a triple-axis crystal spectrometer.[5] Figure 1 gives the energy differential scattering cross section. These data have been corrected for detector response, a measured background including monochromator incoherent scattering, and a measured second-order contamination. A three-point binary average of the data points has been applied.

For comparison with Danner's result, the data have been converted in Fig. 2 to a phonon frequency spectrum according to the one-phonon incoherent scattering approximation, with the Debye–Waller factor set to 1.[6] Calculations show that the difference in the two-phonon contributions for the "cold" and "warm" experiments is small.[7] Hence, for a given phonon energy, the two spectra should nearly coincide. For additional comparison, we have used the Danner spectrum to generate a cross section appropriate to the present experiment. This is the solid curve in Fig. 1. The dashed curve is a similar calculation for the Wunderlich spectrum,[8] derived from a "best fit" to specific-heat data.

We observe that the spectra agree well in the region below 250 cm^{-1}. The present data do not show the large peak at 570 cm^{-1} but show at most only a weak rise near 500 cm^{-1}. As indicated in Fig. 1, such an event should have been easily recognized. The data are more

nearly consistent with the Wunderlich spectrum in the region from 400 to 600 cm^{-1}.

Additional weak structure is evident in our data, including peaks near 160 and 95 cm^{-1}, and probably near 50, 66, 275, and 340 cm^{-1}. This structure persisted through several runs including a different target thickness and different final energy of 0.027 eV. We conclude, therefore, that the structure is probably real and not due to possible beam contamination. We assume that some low-energy events are due to intermolecular coupling, and note that those peaks at 160 cm^{-1} and below are not inconsistent with the approximate model of Tasumi.[9]

* Work supported by the National Science Foundation.

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[3] See, however, the close similarity with weak infrared structure reported by H. A. Willis, R. G. Miller, D. M. Adams, and H. A. Gebbie, Spectrochim. Acta **19**, 1457 (1963).

[4] We are indebted to Danner for providing the target material.

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Notes

Collision-Induced Luminescence of Gases*

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A SERIES of ionization measurements, which indicate that the irradiation of argon by high-energy particles leaves argon atoms in two sets of excited states with energies of approximately 11.5 and 14.5 eV, have been carried out by Hurst and co-workers.[1] Strickler and Arakawa[2] have investigated the α-particle-induced luminescence of argon using spectroscopic techniques, and the present work (which continues an earlier study by LWS) deals with the luminescence induced by 3-MeV electrons. The apparatus used has been described in a previous article.[3]

Before discussing the results it is necessary to establish a label system for argon interactions mentioned by Strickler and Arakawa. Diffuse emissions at about 2200 and 1300 Å have been interpreted in terms of transitions between excited argon dimers Ar_2^* and Ar_2^{**}. We use Ar_2^{**} to denote an excited argon dimer (or one of a set of dimers) constructed from a ground-state argon atom and one excited to one of the complex of levels around 14.5 eV. Similarly, Ar_2^* is used to denote a dimer (or one of a set of dimers) constructed from a ground-state argon atom and one in one of the levels around 11.5 eV. These have been tentatively described[2] in terms of $Ar_2^{**} \rightarrow Ar_2^* + h\nu$ (2200 Å) and $Ar_2^* \rightarrow Ar + Ar + h\nu$ (1300 Å). There is also evidence[4] for $Ar_2^{**} \rightarrow Ar + Ar + h\nu$ (800 Å).

At higher concentrations of nitrogen in argon (>3%), Strickler and Arakawa (SA) observed that the continuum around 2200 Å decreases in intensity and adopts a structured form which becomes more clearly defined with increasing nitrogen concentration (SA Figs. 12, 13). Attempts by us to fit their unassigned emission to second positive and first negative bands of nitrogen were unsuccessful. After our experiments had been performed, it became obvious that the single peaks of SA (Fig. 13) were in fact doublets (extremely low luminescence intensity forced SA to use wide slits) which could readily be assigned to the γ system of NO ($A\,^2\Sigma \rightarrow X\,^2\pi$). The luminescence is well developed in 97% Ar/3% N_2, presumably as a result of oxygen impurity. Further experiments, at the same relative argon concentration using N_2/O_2 mixtures to make up the remaining 3%, showed no detectable level of this emission using 80/20 N_2/O_2, and it appeared that O_2 had to be present only in small amounts for well-developed γ-NO luminescence to appear. The luminescence is extensive and well developed in a 97%-Ar mixture where the remaining 3% was 99/1 N_2/O_2; showing a series of double-headed bands, the most intense originating from $V^1=0$ accompanied with very much weaker development of $V^1=1$. We suggest that this emission arises from the interaction of $B\,^3\pi_g N_2$ and ground-state $X\,^3\Sigma O_2$. At $v=0$ of the nitrogen B state, the proposed reaction is in rough energy balance for production of $V^1=0$ of $A\,^2\Sigma NO$, the upper state of the γ bands. We have rejected the $N\cdot + O_2$ reaction as energy deficient, and the three-body reaction of N and O usually gives β and γ bands (as in the NO titration of N) and a population $V^1=5 \rightarrow 9$ almost exclusively, for $N\,^4S$ and $O\,^3P$ reaction.[5] Other reasons for assignment of the reactant as $^3\pi_g N_2$ are as follows.

(i) Experiments with krypton instead of argon showed equally intense development of the γ system after correcting for the variation in atomic stopping power for 3-MeV electrons. In the krypton case, however, the C state of N_2 cannot be produced by reaction with the krypton system corresponding to the 11.5-eV set in argon. Populations of the $B\,^3\pi_g$ state of N_2 (or $B'\,^3\Sigma_u^-$, which converts to $^3\pi_g$) in the quenching process are the only reactions allowed by the Wigner–Witmer correlation rules.

(ii) Excitation of ground-state NO after production in other reactions can be ruled out as a possibility