Polarization Measurements of Raman Lines

George Glockler and H. T. Baker

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without the assumption of an anomaly characteristic of rubber in general.

A recent communication[5] has presented data which show that the melting range of crystalline rubber is very much dependent on the temperature at which the crystallization takes place. More complete data not yet published show that when crystallization occurs between $-40°C$ and $+10°C$, melting begins at a temperature of from 4° to 7° above that at which the crystals were formed, and the melting continues over a range of from 10° to 30° more. Crystallization is most rapid in the neighborhood of $-20°C$ and occurs to a considerable extent within a few hours. At higher and lower temperatures the times involved are of the order of days.

Ruhemann and Simon unfortunately give little information about rates of heating or cooling during their measurements, but it may be presumed that it required several hours to take the observations in the range in which crystallization is sufficiently rapid to influence their results. This is ample time for appreciable crystallization, which would then take place for the most part between $-20°C$ and $-10°C$. The corresponding melting would then be expected to occur in the region around $0°C$.

In some cases observations were begun at about $-100°C$, but in others, especially where the β-anomaly was under particular investigation, the observations were started at $-20°C$. In the latter cases there was probably even more opportunity for crystallization at temperatures of $-20°C$ and somewhat above.

In two experiments to study the β-anomaly, Ruhemann and Simon held rubber for 5 hours and 12 hours at a "low temperature" (presumably $-20°C$). The specimen held the longer time showed a much larger heat of transition. The anomaly extended in both cases from about $-10°$ to about $+10°C$. Furthermore, the authors state: "In contrast to the α-anomaly, the β-anomaly was not strictly reproducible. Depending on the speed of heating as well as the previous cooling the curve is steeper or flatter. Also the energy, that is the area under the curve, was different in different measurements. The mean value for smoked sheet amounted to about 2 cal. per gram of rubber."

Ruhemann and Simon found no β-anomaly in a specimen of vulcanized rubber. This is in accordance with the observation[6] that only certain types of vulcanized rubber crystallize, when unstretched, and that even in these the rate of crystallization is much less than in unvulcanized rubber. Consequently, the amount of crystallization during the experiment was negligible.

In another part of their paper Ruhemann and Simon present a graph of volume against temperature. The graph clearly shows the effect of crystallization and subsequent melting. From about $-20°$ to $-5°C$ the observations fall farther and farther below the straight line representing the normal thermal expansion. From $-5°C$ to $+8°C$ the observations approach the straight line, and above $8°C$ fall on the line.

The conclusion may then be drawn that the β-anomaly represented merely the melting of crystals formed under the particular experimental conditions of Ruhemann and

Simon. It was usually found near $0°C$ because the crystals were formed between about $-20°C$ and $-10°C$. Below this range and above it crystallization was so slow as to be inappreciable during the time of an experiment.

[1] M. Ruhemann and F. Simon, "A contribution to the knowledge of the physical properties of rubber," Zeits. f. physik. Chemie **A138**, 1 (1928).
[2] N. Bekkedahl, "Forms of rubber as indicated by temperature-volume relationship," J. Research Nat. Bur. Stand. **13**, 411 (1934) RP 717. Reprinted in Rubber Chem. Tech. **8**, 5 (1935).
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[4] L. A. Wood, N. Bekkedahl, and C. G. Peters, "Application of the interferometer to the measurement of dimensional changes in rubber," J. Research Nat. Bur. Stand. **23**, 571 (1939) RP 1253. Reprinted in Rubber Chem. Tech. **13**, 290 (1940).
[5] N. Bekkedahl and L. A. Wood, "Influence of the temperature of crystallization on the melting of crystalline rubber," J. Chem. Phys. **9**, 193 (1941). Reprinted in Rubber Chem. Tech. **14**, 544 (1941).
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Polarization Measurements of Raman Lines

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WE have lately studied the measurements of the depolarization factor of Raman lines. Our experimental arrangement seems to involve some advantages not considered by other investigators. We use the fixed polaroid located between the Raman tube and the spectrograph as employed by Cleveland and Murray.[1] The marked arrow of the polaroid disk is at an angle of 45° to the vertical direction.

The two arcs, the two filters, and one Raman tube are rigidly fastened so that all are parallel and lie in one plane. The first exposure is taken after rotating this plane by an angle of 45° from the horizontal position. The axis of the spectrograph which is also the axis of the Raman tube is the axis of rotation. The second exposure is taken after rotating the apparatus through a 45° angle in the opposite direction from the original horizontal position. The two exposures are therefore taken in positions which differ by a 90° angle. This change in angular position can be carried out with great ease. Moreover arcs, filters, and Raman tube are always in the same relative position, so that the light leaves the arcs and enters the Raman tube in exactly the same place.

For the calibration spectra we employed the continuum obtained from a gas-oxygen flame which could be controlled and varied easily. A rotating sector allowed different intensities to be photographed on the plate. Again ease of manipulation seems to be an important advantage. The use of continuous calibration spectra allows density comparisons at the exact wave-length of a given Raman line. Preliminary results on the depolarization factor for carbon tetrachloride are as follows: 218 cm^{-1} (0.79, 0.80, 0.82); 314 cm^{-1} (0.80, 0.78, 0.86); 459 cm^{-1} (0.24, 0.24, 0.38); 762 and 790 cm^{-1} (0.84, 0.83, 0.86). The results for the first, second, and fourth lines, which have a large depolarization factor check satisfactorily with other investigations.[1] Our values for the third line are high and we expect to investigate this matter further.

[1] F. F. Cleveland and J. M. Murray, Res. Publ. Illinois Inst. Tech. **2**, 1 (1941).