M. M. Sushchinskiĭ. *Raman scattering of light in phase transitions in crystals.* In their scientific work, L. I. Mandel'shtam and G. S. Landsberg gave a great deal of attention to temperature studies. It was therefore natural that they should have investigated Raman spectra thoroughly in a broad temperature range in one of the very first papers on Raman scattering. Their paper[1] reported a study of Raman scattering in quartz, which has a phase transition at 573 °C. They observed curious behavior of one of the Raman lines (frequency 207 cm^{-1}). As the temperature was raised, this line broadened strongly and shifted towards the exciting line, to vanish above the phase-transition point.

It became clear later that this behavior of Raman lines in phase transitions in crystals is of great interest in itself. However, detailed Raman-scattering study of phase transitions began much later, after V. L. Ginzburg, W. Cochran and others[2,3] pointed out interesting aspects of the behavior of individual Raman lines near second-order phase-transition points. According to theory, the frequency of one or more Raman lines should tend to zero with the approach to a second-order phase-transition point, and its intensity should rise sharply. The crystal vibrations corresponding to these Raman lines have come to be known as the "soft mode."

Theoretical studies[2,3] stimulated numerous experimental projects whose purpose was to observe the soft mode. The vibrational spectra of crystals around first- and second-order phase-transition points were being investigated for the most part in connection with the ferroelectric properties of these crystals. A significant increase in the dielectric constant is observed on ferroelectric phase transitions, in agreement with the theoretical results.[2,3] However, attempts to find a Raman line that could definitely be interpreted as a "soft mode" had generally failed. There were only a few isolated cases in which experimental data agreed with the "soft mode" theory (crystals of lead germanate $5PbO \cdot 3GeO_2$,[4] antimony sulfiodide SbSI[5,6] and certain others). These were the factors that led to prominent Brazilian spectroscopist S. P. S. Porto to reject the entire "soft mode" concept.[7]

Research done in recent years has shown that changes in Raman spectra on ferroelectric phase transitions are not always manifested in quite the same way as would be expected on the basis of the original theory, but they do not justify total rejection of the "soft mode" concept. We might point, for example, to recent data obtained by V. S. Gorelik *et al.*[8] in a study of lithium tantalate $LiTaO_3$, lithium niobate $LiNbO_3$, and certain mixed crystals. At low temperatures, the Raman spectra of these crystals have a number of sharp intensity peaks. As the temperature is raised, the lines broaden and overlap one another. With the approach to the phase transition point, the Raman spectrum acquires an increasingly conspicuous "continuum" quality at low frequencies, and this continuum shifts as a whole

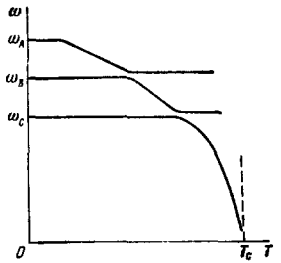

FIG. 1.

toward the exciting line, while its intensity increases.[9] The sharp increase in the dielectric constant, which is contributed to not by a single "soft mode," but by a whole series of vibrations, is explained accordingly.

We draw attention to certain features in the behavior of Raman lines with the approach to a phase-transition point. Not one but several successive vibrations *A*, *B*, and *C* participate in the "softening" process (see Fig. 1). First to soften is vibration *A* with a comparitively high frequency ω_A, which gradually decreases with increasing temperature, approaching the frequency ω_B of vibration *B*. As the frequencies of these vibrations move closer together, they begin to interact strongly. As a result, the frequency of vibration *A* remains constant as the temperature rises further, but the frequency ω_B begins to decrease, i.e., vibration *B* is assuming the role of the "soft mode." Things continue in this way until frequency ω_B approaches the frequency ω_C of vibration *C*. Then vibrations *B* and *C* interact, and vibration *C* continues the "relay" in the frequency decrease. Its frequency rapidly drops nearly to zero, in exact agreement with the "soft mode" theory. This "relay race" of vibrations can be traced clearly in the changes of the Raman spectra of antimony sulfiodide SbSI[5,6] as the pressure is raised (see Ref. 10).

We might also mention the thoroughly studied transition of quartz in which the frequency of one of the lines drops from 207 to 165 cm^{-1} as the temperature rises and then changes no further. A second-order line assumes the role of the "soft mode," its frequency decreasing from 147 cm^{-1} to ~40 cm^{-1} (see Ref. 11).

In view of the interaction of several cyrstal-lattice vibrations with progressive softening of first one and then another, the "soft mode" concept would appear to us to retain its significance as the leading idea for explaining the properties of crystals in second-order phase transitions.

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