AN EXPERIMENTAL STUDY OF THE PHASE TRANSITION IN FERROCENE

J.S. BODENHEIMER and W. LOW
Microwave Division, The Racah Institute of Physics, The Hebrew University, Jerusalem, Israel

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Experiments on the phase transitions and on the disintegration at low temperatures of single crystals and polycrystalline ferrocene are reported. They show that these two are separate phenomena.

Ferrocene $[Fe(C_5H_5)_2]$ crystals undergo violent disintegration into yellowish powder when cooled near liquid nitrogen temperatures. This has been considered to have some connection with a λ-point in the specific heat which has been observed at 163.9°K [1]. Stephenson and Winterrowd have presented a method of retaining very thin crystals down to 77°K [2]. This method has recently been used to obtain the absorption spectrum at 4.2°K [3]. Anomalous narrowing in proton resonance between 115 - 225°K has also been reported [4]. Duecker and Lippincott have observed a pressure induced phase transformation at 11 kbar [5].

This communication reports various investigations on ferrocene which were undertaken in order to obtain additional information about the phase transition and the disintegration. The single crystals were grown from solution in toluence and other solvents.

a) *Differential thermal analysis* (DTA): The phase transition at 164°K was detected, using a DTA apparatus built for this purpose. Through repeated slow cycling the transition proved to be reversible. The single crystals did not "explode" though held for twelve hours at 130°K. However, when the crystals were slowly cooled down to 80°K, the disintegration could be detected by a large momentary temperature gradient, near 110°K (fig. 1a). The exact temperature at which the disintegration occurred dependend on the rate of cooling. The lowest disintegration temperature was observed at 108°K and the highest (using rapid cooling) at 125°K. The disintegration effect itself could not be repeated, even after the powder had been raised to room temperature for several days. Nevertheless, the phase transition at 164°K *was* observed after disintegration, with an intensity reduction of about 40% (fig. 1b). The weakening of the signal can be possibly explained by the lower heat conduction of the powder.

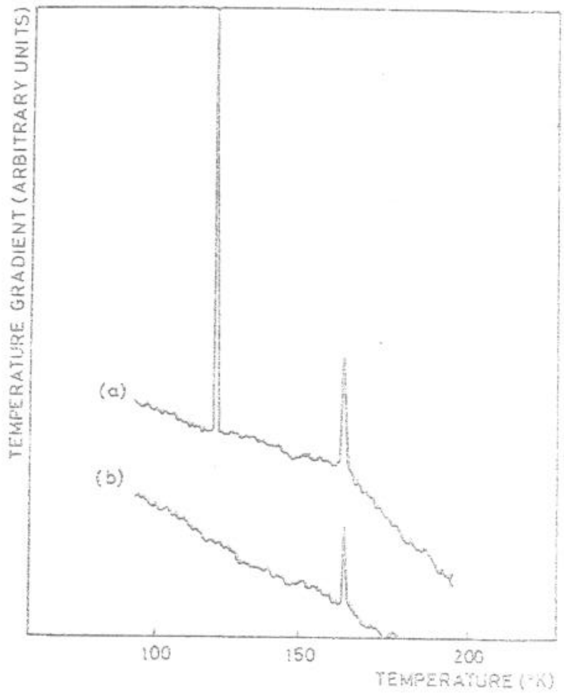

Fig. 1. Differential thermal analysis of ferrocene as function of temperature: a) Single crystals cooled through phase transition and disintegration. b) Same sample after disintegration.

Single crystals grown from powder which resulted from disintegration exhibited similar behaviour as the original crystals using the DTA. These effects were also observed on annealed crystals. Single crystals crushed to polycrystalline powder of less than 0.011" size did *not*, however, disintegrate when cooled to 80°K. Similarly, small single crystals obtained from the dis-

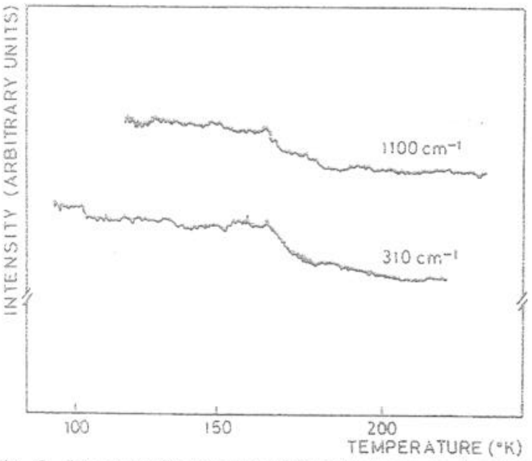

Fig. 2. Integrated intensity of Raman lines as function of temperature.

integration of the large crystal could be cooled to 77°K without further disintegration.

From the above results it is clear that the phase transition at 164°K and the disintegration at 110°K are two *separate* phenomena.

b) *Raman spectra*: Raman spectra of ferrocene single crystals have been reported down to 200°K [7]. The Raman spectrum of a fragment of a disintegrated crystal was found to be identical to that of an untreated single crystal. The general features of the intra-molecular spectrum were unchanged as the fragment was cooled down to 80°K except for narrower line widths which enabled better resolution of the crystal field splitting. However, the intensity of the two strong lines at 310 cm^{-1} (ring-metal stretch) and 1100 cm^{-1} (ring breathing) showed an anomalous temperature dependence near 164°K (fig. 2).

c) *Uniaxial pressure*: Cooling the crystal slowly under applied pressure of the order of 10 bar prevented disintegration. This experiment was done by simply clamping the crystal between two glass plates. Thin single crystals thus treated were only mildly fractured. After removing pressure, these crystals could then be cooled down to 80°K for extended periods without disintegration. Repetitive temperature cycling caused further fracturing.

These experiments seem to indicate domain structure which finally disintegrates into single domain crystallites near 110°K.

A detailed discussion of the experiments described will be published.

References

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