

value agrees with that obtained from spectra taken of the entire sample at an applied pressure of 11 kbar. Using spectral data of the latter type from 0 to 40 kbar, the spectral shift of ferrocene I is determined to be about  $32 \text{ cm}^{-1}/\text{kbar}$  while that of ferrocene III is found to be about  $18 \text{ cm}^{-1}/\text{kbar}$ . This spectral shift is qualitatively in agreement with Weir, Van Valkenburg, and Lippincott and agrees quantitatively with Zahner and Drickamer,<sup>9</sup> except in the region of the phase transformation which they apparently did not observe. The lack of discontinuity in the electronic spectra at the phase transformation seems to be in harmony with Okamoto's inability to detect a transformation by an electrical conductivity method.<sup>1</sup>

The infrared spectral data of Weir, Van Valkenburg, and Lippincott cannot be significantly improved upon since we were unable to take micro-infrared spectra of ferrocene I and III at the phase boundary. The  $1108\text{-cm}^{-1}$  band in ferrocene I is observed to shift to  $1135 \text{ cm}^{-1}$  in ferrocene III, in agreement with the discontinuity reported earlier. This shift was found to be especially sharp or discontinuous if a single crystal of ferrocene is compressed as above. On the other hand, if microcrystalline ferrocene is compressed, the  $1108\text{-cm}^{-1}$  band appears to simply broaden and decrease in intensity. Upon release of the pressure and recompression, the relative intensity of the  $1135\text{-cm}^{-1}$  peak

increases and with further recompressions, the  $1108\text{-cm}^{-1}$  band virtually disappears.

This result suggests that the formation of ferrocene III may be "shear induced," especially since the most evident conversion of ferrocene to ferrocene III is by the rapid compression of a single crystal and microcrystalline ferrocene transforms sluggishly.

A portion of this work was carried out at the National Bureau of Standards, Washington, D.C.

\* Supported in part by grants from the U.S. Army Research Office, Durham, and by a Materials Science Program from the Advanced Research Projects Agency, U.S. Department of Defense.

<sup>1</sup> Y. Okamoto, T. Y. Chang, and M. A. Kantor, *J. Chem. Phys.* **41**, 4010 (1964).

<sup>2</sup> C. E. Weir, A. Van Valkenburg, and E. R. Lippincott, in *Modern Very High Pressure Techniques*, R. A. Wentorf, Ed. (Butterworths, Inc., Washington, D.C., 1962), pp. 51-68.

<sup>3</sup> The designation ferrocene II is reserved for the low-temperature form of ferrocene observed by Weir and Lippincott (private communication).

<sup>4</sup> J. C. Zahner and H. G. Drickamer, *J. Chem. Phys.* **33**, 1625 (1960).

<sup>5</sup> E. R. Lippincott and H. C. Duecker, *Science* **144**, 1119-1121 (1964).

<sup>6</sup> W. A. Bossett and T. Takahashi, *Am. Mineralogist* **50**, 1576 (1965).

<sup>7</sup> J. C. Zahner and H. G. Drickamer, *J. Phys. Chem. Solids* **11**, 92-96 (1959).

<sup>8</sup> M. Freeman, "Effect of Pressure on the Spectrum of Ferrocene," M.S. thesis, University of Maryland, 1965.

<sup>9</sup> J. C. Zahner and H. G. Drickamer, *J. Chem. Phys.* **35**, 375 (1961).