

ther. Accordingly, Eqs. (4) and (8) of our paper¹ should be multiplied by the factor $e_\lambda \cdot (e_\mu \times e_\nu)$.

Finally, we wish to point out three misprints: in Eq. (4) $k_\mu - k_\lambda$ should read $k_\mu - k_\lambda$, Eq. (6) should be multiplied by $-(2\pi)^{3/2}$ and in Eq. (7) p_j should read p_j .

*Work supported by the National Science Foundation and Contract No. SD-69 of the Advanced Research Projects Agency.

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Phase Transformation in Ferrocene*

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(Received 30 June 1966)

EVIDENCE has been presented in this journal¹ by Okamoto, Chang, and Kantor that ferrocene does not have a phase transformation below 20 kbar and reference is made to earlier work of Van Valkenburg and Weir to support this view.

Actually, evidence for the existence of a phase transformation in ferrocene has first presented by Weir, Van Valkenburg, and Lippincott,² although no optical or x-ray identification of the transformation was possible at that time. On occasion we have observed ferrocene in the diamond-anvil, high-pressure cell and found a rather distinct boundary between the ferrocene in the high pressure region (in the center of the cell) and that near atmospheric pressure at the edge of the diamond, (see Fig. 1). We have recently been able to produce the transformation at will and have determined the pressure of the transformation and the optical properties of the two phases.

The formation of ferrocene III³ can be observed most easily in the following experiment. A single crystal of resublimed ferrocene is placed in the diamond-anvil high-pressure cell and the applied pressure is increased to about 20 kbar. As the pressure is applied, the boundary between ferrocene I and ferrocene III can be faintly observed. However, the boundary becomes very distinct upon decreasing the pressure, since as the boundary moves inward toward the center of the cell, ferrocene I crystallizes from ferrocene III in the form of crystallites 1 to 5 μ in diameter. These crystallites can be easily distinguished from the continuous layer of ferrocene in the center. One cannot distinguish the phase transformation boundary if polycrystalline ferrocene is used, but infrared and visible absorption measurements are identical with those obtained with single crystals as above if sufficient time is allowed to reach equilibrium.

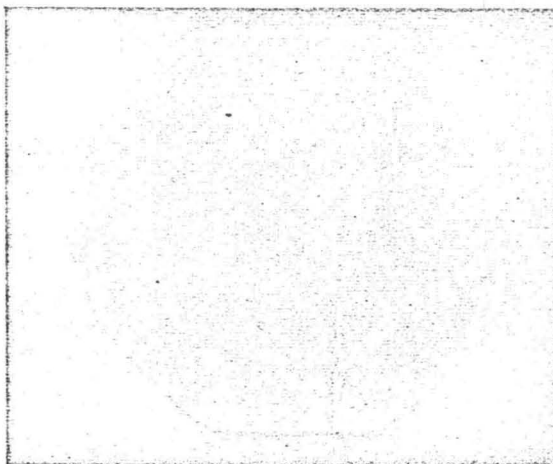


FIG. 1. View of ferrocene (100 \times) in diamond-anvil pressure cell at 16 kbar (applied pressure) showing layer of ferrocene III in center and polycrystalline ferrocene I around it. The artifact is a result of handling and unrelated to the observed phenomenon.

X-ray identification of ferrocene III has not been possible in the diamond-anvil high-pressure cell because of the low mass of the atoms, the small amount of the sample (compared with the mass of the diamonds) and the fact that we have not as yet been able to grow ferrocene III single crystals in a uniform pressure field.

Two methods have been employed to evaluate the pressure of the transformation. In one experiment, a crystallite of nickel dimethylglyoxime was placed between the ferrocene crystal and the diamond so that the application of pressure gave a ferrocene matrix with a few suspended crystallites of nickel dimethylglyoxime. The position of the absorption band in nickel dimethylglyoxime at the ferrocene (I-III) boundary permitted an assignment of pressure using the data of Zahner and Drickamer⁴ and confirmed in the diamond-anvil high-pressure cell by Lippincott and Duecker.⁵ In this manner, the transformation pressure was determined to be 11.5 ± 0.5 kbar.

In another approach, the transformation pressure was compared with the transformation pressure of mercuric iodide by the simultaneous compression of hemicylindrical disks of mercuric iodide and ferrocene. A comparison was then made of the transformation pressures by the method of Bassett and Takahashi.⁶ Assuming a nearly linear pressure gradient in the region of the transformation, we calculate a transformation pressure of 11.0 ± 0.7 kbar using Drickamer's mercuric iodide transformation pressure of 13 kbar.⁷ These transformation pressures are not far from that predicted by Weir, Van Valkenburg, and Lippincott, or that found by Freeman in a fully hydrostatic environment.⁸

The phase transformation presents no discontinuity in the absorption band at $23\,100\text{ cm}^{-1}$. Spectra taken from microsections of ferrocene I and III at the phase boundary both have maxima at $23\,450 \pm 50\text{ cm}^{-1}$. This

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,⁹ 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.¹

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-cm^{-1} band in ferrocene I is observed to shift to 1135 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-cm^{-1} band appears to simply broaden and decrease in intensity. Upon release of the pressure and recompression, the relative intensity of the 1135-cm^{-1} peak

increases and with further recompressions, the 1108-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.

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

² 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.

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

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

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

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

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

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