APPENDIX

Quadrupole Splitting

The behavior of the ferric and ferrous quadrupole splittings was also examined as a function of pressure. Since the ferric ion has a spherically symmetric *d* electron shell, its quadrupole splitting is initially rather small. Changes with pressure reflect predominantly the changes in electric field gradient because of local deviations from cubic (octahedral) symmetry. Changes in the ferrous quadrupole splitting are more difficult to analyze since the occupation of the asymmetric *d* electron shell is the primary factor (leading to the large initial quadrupole splitting) and the effect of pressure on this factor is less well-defined. There is a general tendency for the ferric quadrupole splitting to increase over the pressure range (see Table II). For clarity of presentation, the 12 derivatives have been divided into two groups according to structural considerations, rather than the three classes based on electronic factors. Group I consists of the asymmetrically substituted chelates BTFA(8), FTFA(6), TTFA(7), BA(4), and TFACA(5) which are listed in decreasing order of their quadrupole splittings at the highest pressures. Group II consists of the symmetrically substituted derivatives DBM(2), NACA(11), ACA(1), EACA(12), DPM(3), MACA(9), and PACA(10), also listed in decreasing order. At low pressures there is no distinction between the groups with the quadrupole splittings for all the derivatives lying between 0.63–0.91 mm/sec at 20 kbars. As the pressure increases there is a definite tendency for the asymmetric derivatives (Group I) to exhibit larger quadrupole splittings although there is measurable overlap of the groups even at the highest pressures. The high pressure range of Group I is 1.60–1.85 mm/sec; Group II falls in the region 1.42–1.68 mm/sec. Thus the electric field gradient must increase slightly more for the asymmetrically substituted derivatives than for the symmetrically substituted ones.

There was no obvious classification of the ferrous quadrupole splittings into smaller subgroups, either on structural or electronic grounds. Although the ferrous quadrupole splittings generally show more scatter than the ferric values, it is still possible to establish a range of 2.0–2.5 mm/sec at 20 kbars and a general decrease in splitting of the order of 0.1 mm/sec over the pressure range. In many compounds it appears that the data go through shallow minima between 80–120 kbars.

---

* This work was supported in part by the U.S. Atomic Energy Commission under Contract AT(11-1)-1198.

[1] P. de Brunner, R. W. Vaughan, A. R. Champion, J. Cohen, J. Moyzis, and H. G. Drickamer, Rev. Sci. Instr. **37,** 1310 (1966).

[2] R. A. Fitch, T. E. Slykhouse, and H. G. Drickamer, J. Opt. Soc. Am. **47,** 1015 (1957).

[3] H. G. Drickamer and A. S. Balchan, in *Modern Very High Pressure Techniques*, edited by R. H. Wentorf, Jr. (Butterworths, London, 1962).

[4] H. G. Drickamer, V. C. Bastron, D. C. Fisher, and D. C. Grenoble, Solid State Chem. **2,** 94 (1970). (This paper contains references to papers published before 1970.)

[5] D. C. Fisher and H. G. Drickamer, J. Chem. Phys. **54,** 4825 (1971).

[6] D. C. Grenoble and H. G. Drickamer, J. Chem. Phys. **55,** 1624 (1971).

[7] D. C. Grenoble, C. W. Frank, C. B. Bargeron, and H. G. Drickamer, J. Chem. Phys. **55,** 1633 (1971).

[8] C. B. Bargeron, M. Avinor, and H. G. Drickamer, Inorg. Chem. **16,** 1338 (1971).

[9] C. B. Bargeron and H. G. Drickamer, J. Chem. Phys. **55,** 3471 (1971).

[10] C. P. Slichter and H. G. Drickamer, J. Chem. Phys. (to be published).

[11] R. A. Marcus, Ann. Rev. Phys. Chem. **15,** 155 (1964).

[12] R. A. Marcus, J. Chem. Phys. **43,** 1261 (1965).

[13] N. S. Hush, *Progress in Inorganic Chemistry* **8,** 357, edited by F. A. Cotton (Interscience, New York, 1967).

[14] N. S. Hush, Electrochim. Acta **13,** 1005 (1968).

[15] A. Hantzsch and C. H. Desch, Annalen **323,** 1 (1902).

[16] D. N. Sen and N. Thankarajan, Indian J. Chem. **3,** 215 (1965).

[17] J. W. G. Wignall, J. Chem. Phys. **44,** 2462 (1966).

[18] H. C. Brown and Y. Okamoto, J. Am. Chem. Soc. **80,** 4979 (1958).

[19] S. M. Schildcrout, R. G. Pearson, and F. E. Stafford, J. Am. Chem. Soc. **90,** 4006 (1968).

[20] G. M. Bancroft, C. Reichert, and J. B. Westmore, Inorg. Chem. **7,** 870 (1968).

[21] G. M. Bancroft, C. Reichert, J. B. Westmore, and H. D. Gessor, Inorg. Chem. **8,** 474 (1969).

[22] C. Reichert and J. B. Westmore, Inorg. Chem. **8,** 1012 (1969).

[23] C. Reichert, G. M. Bancroft, and J. B. Westmore, Can. J. Chem. **48,** 1362 (1970).

[24] C. Reichert and J. B. Westmore, Can. J. Chem. **48,** 3213 (1970).

[25] H. F. Holtzclaw, Jr., R. L. Lintvedt, H. E. Baumgarter, R. G. Parker, M. M. Bursey, and P. F. Rogerson, J. Am. Chem. Soc. **91,** 3774 (1969).

[26] H. F. Holtzclaw, Jr., K. W. R. Johnson, and F. G. Hengeveld, J. Am. Chem. Soc. **74,** 3776 (1952).

[27] H. F. Holtzclaw, Jr., A. H. Carlson, and J. P. Collman, J. Am. Chem. Soc. **78,** 1838 (1956).

[28] E. R. Nightingale, Jr., and H. F. Holtzclaw, Jr., J. Am. Chem. Soc. **81,** 3523 (1959).

[29] R. L. Lintvedt, H. D. Russell, and H. F. Holtzclaw, Jr., Inorg. Chem. **5,** 1603 (1966).

[30] N. E. Erickson, in *Mössbauer Effect and Its Chemical Applications*, edited by P. F. Gould (American Chemical Society, Washington, 1967).

[31] H. G. Drickamer and J. C. Zahner, Advan. Chem. Phys. **4,** 161 (1962).

[32] H. G. Drickamer in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic, New York, 1965), Vol. 17, p. 1.

[33] S. C. Fung and H. G. Drickamer, J. Chem. Phys. **51,** 4353 (1969).

[34] R. L. Belford, A. E. Martell, and M. Calvin, J. Inorg. and Nucl. Chem. **2,** 11 (1956).

[35] F. Hashimoto, J. Tanaka, and S. Nagakura, J. Mol. Spectry. **10,** 401 (1963).

[36] L. S. Forster, J. Am. Chem. Soc. **86,** 3001 (1964).

[37] R. H. Holm and F. A. Cotton, J. Am. Chem. Soc. **80,** 5658 (1958).

[38] D. W. Barnum, J. Inorg. and Nucl. Chem. **21,** 221 (1961).

[39] D. W. Barnum, J. Inorg. and Nucl. Chem. **22,** 183 (1961).

[40] C. K. Jorgensen, Acta Chem. Scand. **16,** 2406 (1962).

[41] Y. Murakami and K. Nakamura, Bull. Chem. Soc. Japan **39,** 901 (1966).

[42] R. R. Singh and R. Sahai, Australian J. Chem. **22,** 1169 (1969).

[43] C. K. Mathews, J. Inorg. and Nucl. Chem. **31,** 2853 (1969).

[44] R. Grobelny, B. Jezowska-Trzebiatoswka, and W. Wojciechowski, Bull. Acad. Polon. Sci. **17,** 285 (1969).

[45] I. Hanazaki, F. Hanazaki, and S. Nagakura, J. Chem. Phys. **50,** 265 (1969).

[46] I. Hanazaki, F. Hanazaki, and S. Nagakura, J. Chem. Phys. **50,** 276 (1969).

[47] E. A. Magnuson, R. A. Thomson, and A. G. Wedd, Chem. Commun. 842 (1969).

[48] R. L. Lintvedt and L. K. Kernitsky, Inorg. Chem. **9,** 491 (1970).

[49] D. R. Stephens and H. G. Drickamer, J. Chem. Phys. **30,** 1518 (1959).

[50] R. S. Mulliken, J. Am. Chem. Soc. **74,** 811 (1952).

[51] R. S. Mulliken, J. Phys. Chem. **56,** 801 (1952).