along the mirror twin and twist twin composition planes of the two types of platelets.

Rapid diffusion along the blade length and slow diffusion across the blade width are consistent with the crystallographic symmetry of the blade, and can explain the growth shape. Similarly, the surface diffusion coefficient for a twist grain boundary on the basal plane should be isotropic. It is likely, however, that the unknown structures at the bases of all these growths determine their breadths. Thicknesses are probably determined by the growth mechanisms at the growth sites, which are at the growing tips and edges.

Short-circuit diffusion in gas–metal and solid state reactions in general must be all-important at temperatures where lattice diffusion rates are small. The $\alpha$-$Fe_2O_3$ growths illustrate dramatically the unexpected extremes to be expected where short-circuit diffusion paths are involved.

This work was supported in part by a US Office of Naval Research contract.

R. L. Tallman
E. A. Gulbransen

Westinghouse Research Laboratories,
Pittsburgh, Pennsylvania.

[1] Gulbransen, E. A., and Copan, T. P., Disc. Faraday Soc., 28, 229 (1959).
[2] Gulbransen, E. A., Mem. Sci. Rev. Met., 62, 253 (1965).
[3] Tallman, R. L., and Gulbransen, E. A., J. Electrochem. Soc., 114, 1227 (1967).
[4] Gulbransen, E. A., and Tallman, R. L., Chemical Physics of Surface Reactions of Metals, AD-653 723 (Clearinghouse, Springfield, Virginia, 1967).
[5] Tallman, R. L., and Gulbransen, E. A., J. Electrochem. Soc. (in the press).
[6] Takagi, R., J. Phys. Soc. Japan, 12, 1212 (1957).
[7] Hagel, W. C., Trans. Met. Soc. A.I.M.E., 236, 179 (1966).
[8] Coble, R. L., J. Amer. Ceram. Soc., 41, 55 (1958).

# Mössbauer Effect of Thulium Compound

In recent years the Mössbauer effect has been used for the studies of hyperfine interactions in salts and intermetallic compounds of thulium[1-4].

With this technique we have learnt more about the structure of thulium chelates. We have taken the known C-$Tm_2O_3$ type structure as a model and assumed that $\Delta R/R$, the difference in nuclear radius between the excited and the ground state, is positive. The natural 100 per cent abundant [169]Tm has a 8·42 keV transition from the 3/2 state to the 1/2 ground state. Table 1 shows the Mössbauer parameters of the thulium compounds under study. Thulium benzoate, the acetylacetonate trihydrate, the oxinate, the anhydrous fluoride and the anhydrous thulium chloride were prepared according to refs. 5–9, respectively.

The gamma resonance absorption was measured as a function of relative velocity between source and absorber. Spectra were taken by a drift-free Mössbauer spectro-meter[10] in the constant velocity mode. The measurement involved a 50 mCi erbium fluoride source with a 4·6 mg/$cm^2$ aluminium window, supplied by New England Nuclear Corporation. Each absorber, of thickness 8 mg of thulium/$cm^2$, was enclosed between beryllium windows. Spectra were taken at 298° K and 77° K.

For the oxide and complex compounds the shapes of the curves are similar. They consist of three lines in which the central peak is more intense than the two outer peaks of equal intensity. This suggests that the arrangement of the chelate donor atoms around the trivalent thulium ion is similar to that of the oxide which is known to have the C-$M_2O_3$ type structure[11], in which the metal ions have two kinds of co-ordination group. The two non-equivalent metal ions give rise to three peaks, the central and more intense unsplit peak corresponding to the symmetrical cubic site. It is of interest that as the temperature changes from 298° K to 77° K the resonant absorption intensity for the outer peaks increases markedly whereas the central peak intensity is almost unchanged. Furthermore, the reversal of the direction of magnitude of the splittings in the oxinate as compared with the oxide and other chelates supports the view[12] that the nature of the change of $\Delta$Eq depends on the ligands. Whether the three water molecules in the acetylacetonate are co-ordinated to the metal ion is still uncertain. Comparison of the spectrum of the anhydrous thulium acetylacetonate with that of the trihydrate would certainly be of interest.

The spectra of the anhydrous fluoride and chloride show a doublet at 298° K and 77° K. That these two halides have different structures was shown in the significantly different Mössbauer spectra. The quadrupole split peaks for the chloride are equal in area, while those of the fluoride are quite asymmetric, indicating that the Debye–Waller factor may be very anisotropic in the fluoride but not in the chloride. The quadrupole splitting indicating an electric field gradient at the nuclear site results not only from the distorted partially filled $4f$ electron shell of the thulium ion, but also from the distorted closed electron shells.

The sign of $\Delta R/R$ is of interest to the Mössbauer spectroscopist. In Table 1 the chemical shift of the fluoride (1·2) is less than that of the chloride (1·7). An ionic model may be assumed for the halides because magnetic susceptibility measurements show that covalency is small; and because the fluoride is more electronegative than the chloride the electron density at the nucleus of the thulium ion seems to be less in the former than in the latter. This suggests that $\Delta R/R$ is positive. The fact that the structures are different does not allow an unambiguous assignment of $\Delta R/R$. Further work is in progress to obtain definitive evidence of the sign of $\Delta R/R$.

C. I. Wynter
C. H. Cheek
M. D. Taylor
J. J. Spijkerman

Agricultural and Technical College of
North Carolina,
Howard University, and
US National Bureau of Standards.

[1] Barnes, R. G., Mössbauer, R. L., Kankeleit, E., and Poindexter, J. M., Phys. Rev., 136, A175 (1964).
[2] Cohen, R. L., Phys. Rev., 134, A94 (1964).
[3] Mössbauer, R. L., in Proc. Third Intern. Conf. Me., 362.
[4] Nowik, I., Mössbauer Effect Methodology, 2 (Plenum Press, 1966).
[5] Taylor, M. D., Carter, C. P., and Wynter, C. I., J. Inorg. Nucl. Chem. (in the press).
[6] Stites, J., McCarty, C., and Quill, L., J. Amer. Chem. Soc., 70, 3142 (1948).
[7] Mannelli, G., Atti Tenth Cong. Intern. Chem., 2, 718 (1938).
[8] Poindexter, J. M., thesis, California Institute of Technology (1964).
[9] Taylor, M. D., and Carter, C. P., J. Inorg. Chem., 24, 387 (1962).
[10] Ruegg, F. C., Spijkerman, J. J., and Devoe, J. R., Rev. Sci. Instr., 36 (3), 356 (1965).
[11] Wells, A. F., Structural Inorganic Chemistry, third ed., 465 (Clarendon Press, Oxford, 1962).
[12] Spijkerman, J. J., Ruegg, F. C., and May, L., Mössbauer Effect Methodology, 2 (Plenum Press, 1966).

Table 1. MÖSSBAUER PARAMETERS FOR THULIUM COMPOUNDS

| Compound* | T °K | Quadrupole splitting of the cubic site | Quadrupole splitting $\Delta$Eq (cm/s)† | Quadrupole splitting of the non-cubic site | ‡Chemical shift $\delta$ (cm/s)† |
|---|---|---|---|---|---|
| $TmF_3$ | 298 | | 2·5 | | 1·2 |
| | 77 | | 3·3 | | 1·7 |
| $TmCl_3$ | 298 | | 2·5 | | 3·7 |
| | 77 | | 1·7 | | 4·2 |
| $Tm_2O_3$ | 298 | 0·0 | | 3·3 | 0·0 § |
| | 77 | 0·0 | | 6·6 | 0·0 § |
| $Tm(benzoate)_3$ | 298 | 0·0 | | 8·3 | 0·0 § |
| | 77 | 0·0 | | 12·5 | 0·0 § |
| $Tm(oxinate)_3$ | 298 | 0·0 | | 11·6 | 0·0 § |
| | 77 | 0·0 | | 6·6 | 0·0 § |
| $Tm(acac)_3.3H_2O$ | 298 | 0·0 | | 6·6 | 0·0 § |
| | 77 | 0·0 | | 10·6 | 0·0 § |

\* All compounds gave satisfactory analytical data.
† Standard error ± 0·2 cm/s.
‡ Chemical shifts reported with respect to source.
§ Chemical shifts of cubic and non-cubic sites within experimental uncertainty.