

Fig. 4. The transition enthalpies for pure MgSiO<sub>3</sub>. All data are referred to the enthalpy of the  $\alpha$ - $\beta$ -quartz transition (= 86 cal/mole) according to MAJUMDAR *et al.* (1964).

against the fields of the high-volume phases high-clinoenstatite and protoenstatite which finally will vanish. These relations are presented schematically in fig. 3. Fig. 4 gives the transition enthalpies for pure MgSiO<sub>3</sub>.

The presence of ferrous iron affects the stability of  $MgSiO_3$  in the same way as increasing pressure, causing a marked increase in thermal stability of the rhombic enstatite relative to the high-temperature phases highclinoenstatite and protoenstatite. At a content of 25 mole% of FeSiO<sub>3</sub> the orthopyroxene melts without any previous polymorphic transition (SCHWAB, 1967). However, there are some indications from the measured transformation enthalpies, that the field of the rhombic enstatite might also be extended against the field of low-clinoenstatite to lower temperatures. This assumption is supported by the high pressure experiments of AKIMOTO *et al.* (1965) in pure FeSiO<sub>3</sub>.

The synthesis of orthopyroxenes at 1 atm is easily achieved in the system  $MgSiO_3$ -FeSiO\_3 if it is performed under partial pressures of oxygen which preserve all iron in the bivalent state. It is also possible (as in LiF-containing systems) to demonstrate the reversibility of the transition from high-clinoenstatite to enstatite: slow cooling will lead to enstatite in an exothermal transformation, rapid cooling or quenching will lead to low-clinoenstatite in an exothermal, but at first metastable reaction (fig. 3). e

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## Conclusions

Contrary to previous results the existence has to be assumed of at least one more high-temperature modification of MgSiO<sub>3</sub>. This polymorph is not identical with the high-clinoenstatite described by PEROTTA and STEPHENSON (1965) especially in Ca-containing products.

Moreover there is the very important result, that  $Fe^{2+}$  will influence the polymorphism of MgSiO<sub>3</sub> in the same sense as pressure in the high temperature region. It is remarkable that the maximum stability of the rhombic phase exists at 1 atm at a content of about 25 mole% FeSiO<sub>3</sub> in the system MgSiO<sub>3</sub>-FeSiO<sub>3</sub>.

The structure determination of the high-clinoenstatite modification described here will probably be still more difficult than with protoenstatite, where it is possible to synthetize stabilized single crystals out of talc (LINDEMANN, 1951). Because high-clinoenstatite has its

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