Clark has added some useful data to the authors' original comment on nickelian mackinawite (Vaughan, 1969), especially by his work on cobalt-rich phases.

Recently, the author and M. S. Ridout (unpublished) have gained some insight into the nature of mackinawite through the study of Mössbauer spectra of the pure synthetic iron end member at 300°, 77° and 4.2°K. These spectra, with their very low isomer shifts and absence of quadrupole and magnetic hyperfine interactions even at low temperatures, suggest extensive delocalisation of electrons in mackinawite. On the basis of X-ray powder data, Berner (1962) ascribed to mackinawite the structure of tetragonal PbO with sulphur occupying the lead positions and iron the oxygen positions. This is a very unusual structure, with layers of metal cations tetrahedrally coordinated to sulphur layers above and below resulting in a Fe—S—S—Fe layer structure. The close metal-metal distances (2.6 Å) in the x and y directions in the layers suggest considerable overlap of metal ‘d’ orbitals which would account for the Mössbauer spectra and the absence of a magnetic moment for iron in neutron diffraction experiments (Bertaut et al., 1965).

The structure of mackinawite can probably accommodate cations in additional layers between S—S layers in tetrahedral coordination with sulphur. This would explain reported Fe:S ratios in excess of 1:1. Also, such additional cations would tend to be more prevalent in phases formed (or synthesised) at low temperatures. Such nonstoichiometry should affect the value of the c cell parameter and may be the origin of the high values in synthetic FeS. It encourages caution in correlations of composition and cell parameters.

Extensive overlap of metal ‘d’ orbitals in the x and y directions sug-
gests that the $a$ cell dimension is more dependent on the metallic radius of the cation. Only minor variation would be predicted with substitution of other cations, perhaps a slight decrease Fe$>$Co$>$Ni, but present data are inadequate to confirm this. Unfortunately, ambiguities still remain over the assignment of a composition to the cell-size determination of Kouvo et al. (1964), although none of the alternative interpretations is contrary to the proposed trend in cell-size variation with composition.

Hardness data related to compositional and cell-size variations are interesting but more determinations for different orientations and compositional ranges are required. Although Clark advocates hardness determinations on selected crystal faces, the exact relationship between these three parameters for a particular face is also uncertain.

Mackinawite is clearly capable of accommodating a wide range of metal cations with a metallic radius close to iron. The extremely unusual stereochemistry of sulphur probably contributes to the instability of mackinawite. Clearly this very unusual mineral justifies detailed mineralogical and chemical studies. Until more data are available, caution should be exercised in pronouncements made on the basis of present data.

References