

Science (1964) 145, 1189) or a mirror plane (Rouxhet et al. Clay Min. (1977) 12, 171); as the interlayer space in kaolinite is more asymmetric than in dickite. This new evidence allowed us to take part in the discussion concerning the nature of cohesion of kaolinite layers (Cruz et al., Int. Clay Conf., Madrid (1972) 1, 59; Wieckowski & Wiewiora, Clays Clay Min. (1976) 24, 219). The shift of IR stretching bands of hydroxyls may be the result of interaction of the hydroxyls and the crystal field, and in this case cannot serve as a measure of the energy of a hydrogen bridge as mentioned in the references above. In our study, these energies are found to be 2.5, 1.5 and 2.5 Kcal for hydroxyls H2, H3 and H4 with the help of Brown's work (Acta Cryst. (1976) A32, 24). The calculations show that the crystal loses 2 Kcal/mole $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$ after turning the OH vectors from the positions with minimum electrostatic energy to the experimental positions. Thus, the total gain by the appearance of hydrogen bridges is about 4.5 Kcal/mole. On the other hand, the dependence of electrostatic attraction on the expansion of interlayer space was obtained. In the simplest case of equally expanded interlayers, the electrostatic part is an order more compared to the hydrogen bridges if the increase of separation distance reaches 0.5 Å. More complex variants of the expansion will be also discussed.

08.4-19 THREE DIMENSIONAL MODULATED STRUCTURE OF DIGENITE, $Cu_{6.9}Fe_{0.1}S_4$. By A. Nakano*, Y.

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Digenite, $Cu_{6.9}Fe_{0.1}S_4$, is typical 5a-A type. The apparent space group is Fm3m and the cell edge, a , is 27.78(1) Å. The superstructure was analyzed using the intensity data collected by 4-circle diffractometer. A method for the analysis using modulation functions was developed and successfully applied to solve the structure of 5a-A type of digenite. The apparent cubic symmetry was explained by the coherent twinning of four equivalent domains with rhombohedral symmetry. The face-centered unit cell contains 1000 tetrahedral sites among close packed sulfur atoms. Seven eighths of them are occupied by metal atoms but one eighth are left unoccupied. The vacancies concentrate around each lattice point in the cell. Metal atoms in the neighboring sites to vacancies slightly move toward vacancies. The vacancy concentration was first described by density modulation and the behavior of metal atoms by shift modulation and then the distribution of the vacant tetrahedra was determined. The final weighted and unweighted R values are 0.13 and 0.23, respectively, for 344 intensity data, within the range $\sin\theta/\lambda < 0.4$.

08.4-20 THE CRYSTAL STRUCTURE OF THE HOLLANDITE-TYPE PHASE OF SYNROC B BETWEEN 20°C AND 1060°C. By T. M. Sabine, N.S.W. Institute of Technology, Sydney, Australia and A. W. Hewat, Institut Laue-Langevin, Grenoble, France.

Synroc B, a suggested repository for high level nuclear waste, has components which are synthetic hollandite, perovskite and zirconalite.

The crystal structure of the hollandite phase $BaAl_2Ti_6O_{16}$ has been determined by neutron-diffraction powder methods over a range of temperatures.

Over this temperature range:

1. Thermal expansion is linear with temperature and almost isotropic.
 $\alpha_a = 10.34 \pm 0.05 \times 10^{-6}$,
 $\alpha_c = 11.26 \pm 0.05 \times 10^{-6}$
2. There are no changes in the fractional atomic co-ordinates.
3. The temperature factors of all atoms are essentially isotropic.
4. The diffraction Debye temperature is 581 ± 16 K.
5. The amplitude of vibration of the barium atoms is anomalously high.

08.4-21 AN AUTOMATED X-RAY-DIFFRACTION METHOD FOR THE ROUTINE MINERALOGICAL ANALYSIS OF DRILLING CORES. By C.M. Shepperd and T.J. Laker, British Gas Corporation, London Research Station, London, England.

Phase analysis of minerals in the numbers required for geological surveys is laborious and time consuming whether carried out by X-ray diffraction or point-counting methods. Recent advances in the approach to quantitative X-ray analysis (F.H. Chung, J. Appl. Cryst. (1974) 7 519) have simplified calibration procedures and made this approach more attractive, especially as data acquisition and processing can be automated. We have developed a method for routine analysis of the main minerals in drilling cores which gives results comparable in accuracy and precision to point counting of thin sections, but which is far quicker.

Our method is based on the "matrix-flushing" approach of Chung. Reference intensity ratios for a dozen or so commonly encountered minerals were determined with respect to boehmite ($\alpha-Al_2O_3 \cdot H_2O$) as internal standard or "flushing agent". To allow for the possibility of unexpected and/or amorphous phases, 10% boehmite was added to the rock samples. Intensity data were collected on magnetic tape for subsequent computer processing. Smoothing of the data was found to be necessary for a satisfactory background fit; peaks are recognised and located by a flexible peak search routine in which certain parameters can be varied to suit the quality of the data. Concentrations are derived from measured peak areas by attributing them to the components of interest. Rather narrow d-value limits for the non-clay minerals are allowed (because of overlap problems) but wider limits were set for the clay minerals.

Results on synthetic mineral mixtures indicated an average relative error of up to 5%. For drilling cores it is slightly larger but comparable with point counting.