an R-value of 6.5 %. The positions of the hydrogen atoms could not be determined with the present set of data.

Table 2 gives atomic coordinates and temperature factors with their standard deviations. From these coordinates a Mn—O distance of 2.207 Å with a standard deviation of 0.006 Å is calculated. This Mn—O distance is comparable with the Mn—O distance 2.22 Å, which is calculated from the unit cell parameter 4.445 Å reported for MnO.[7] Å radius of 0.68 Å is calculated for the Mn^{2+} ion using the value of 1.53 Å for the ionic radius of OH^-, and a radius of 0.82 Å is obtained when using the value of 1.40 Å for O^{2-} (Pauling). Apparently the concept of ionic radius for Mn^{2+} is inadequate. From an investigation of magnetic scattering of neutrons in MnO the radial distribution of the electrons in the 3*d*-shell of the Mn^{2+} ion was calculated by Shull, Strauser and Wollan [8] and a maximum of the electron radial density was found in the vicinity of radius 0.6 Å.

Acknowledgements. The author wishes to thank Statens Almindelige Videnskabsfond for placing the high pressure bomb at the author's disposal. Miss R. Grønbæk and Mr. J. Danielsen are thanked for the use of their computer programmes, and Mr. S. J. Jensen, Department of Technology, The Royal Dental College, Aarhus, is thanked for measuring the optical density of the powder pattern.

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Received August 30, 1965.

On the Structure of the Spinel $CuMn_2O_4$

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Most spinels AB_2O_4, where A represents a divalent ion and B manganese ions, are tetragonal because of the distorting tendency showed by octahedrally coordinated Mn^{3+} ions. $CuMn_2O_4$, which is of the above mentioned type if Cu is supposed to be divalent has, however, $c/a = 1$. Dunitz and Orgel [1] have advanced the hypothesis that this should be due to the cooperating effect of the two Jahn-Teller ions, Cu^{2+} and Mn^{3+}, which according to an X-ray powder investigation by Sinha *et al.*[2] are distributed so as to give a normal spinel. The inversion parameter λ, as defined by the formula $[Mn_\lambda Cu_{1-\lambda}]_{tetr}[Cu_\lambda Mn_{2-\lambda}]_{oct}O_4$ is thus equal to 0. According to those authors this value is independent of temperature. The oxygen positional parameter was determined by trial and error methods as $u = 0.267$ (or 0.392, if another origin is chosen).

The result of an X-ray powder study by Zaslavskii *et al.*[3] shows, however, that $CuMn_2O_4$ is not a normal spinel but partially inverted, with the inversion parameter λ within the limits $0.67 \leq \lambda \leq 1$. A more precise determination of λ was considered impossible "in view of the considerable superposition of reflections and the similarity in scattering factor of the copper and manganese atoms". The oxygen parameter u was assumed to have the ideal value of 0.250 (0.375).

A further value of the inversion parameter λ has been reported by Delorme [4] who derived $\lambda = 0.34$ from the ratio of the intensities of the two powder reflections 400 and 422. This value was found to be independent of temperature.

The results obtained by Larson *et al.*[5] from electrical conductivity and magnetic data on $NiMn_2O_4$, which indicate that manganese is partially present as Mn^{2+} and Mn^{4+}, suggest that this may also be the case in $CuMn_2O_4$. From this point of view a detailed structural study of $CuMn_2O_4$ was considered desirable and was undertaken within a research program

conducted at this Institute on the structural properties of spinels and related compounds. This note will give some results obtained so far.

The samples of $CuMn_2O_4$ used in the present study have been prepared by prolonged heating of equimolar mixtures of CuO and Mn_2O_3 in sealed evacuated silica tubes at temperatures varying between 800°C and 1050°C. The samples were cooled from the heating temperature either by quenching or by lowering the temperature at a rate of about 6°C/h. The X-ray powder patterns of the quenched samples showed sharp diffraction lines while the patterns given by the slowly cooled samples were rather diffuse. The dimension of the unit-cell edge, which could be derived from the latter photographs is not very accurate because of the diffuseness of the lines but is significantly shorter than that for the quenched samples by several hundredths of an Ångström. Thus the cell edge for a sample quenched from 1050°C was found to be 8.373 Å while it had the value 8.33_5 Å if the temperature was slowly lowered. A similar difference was also observed by Sinha and co-workers.[2]

Still lower values of the unit-cell parameter, *viz.* 8.32 Å have resulted from preliminary experiments involving heating of a spinel sample in air for a couple of days and then slowly lowering the temperature as described above.

When discussing the cause of the difference between the cell parameters of the samples prepared in the absence of air two mechanisms suggest themselves in the first place, *viz.* a change in the inversion parameter with temperature and a change in the distribution of valencies of the manganese ions according to $2Mn^{3+} = Mn^{2+} + Mn^{4+}$.

A single crystal with $a = 8.373$ Å was obtained from a sample finally heated for 45 days at 1050°C and quenched from that temperature. It was used for collecting three-dimensional data within a complete octant of the reciprocal lattice out to $2\Theta = 90°$, using Nb-filtered Mo$K\alpha$ radiation and a G. E. Single Crystal Orienter equipped with a scintillation detector and a pulse height discriminator. In all 489 reflections with observable intensity were measured of which 125 were independent. With these data a least-squares refinement of the oxygen positional parameter and the three vibrational parameters was started. The inversion parameter λ could not be refined with the program used [6] and a "best value" for this was obtained by a stepwise variation of the Cu/Mn ratio in the tetrahedral and octahedral positions respectively until a minimum in the standard deviations of the refined parameters and in the reliability index R was obtained. In this way a value of $\lambda = 0.4_2$ was arrived at. With this λ value the oxygen positional parameter was equal to $u = 0.263_4$ (0.388_4). The corresponding R walue was then 0.053. In order to make possible a further refinement of the λ parameter a special version of a least-squares program is now being prepared. The possibility of λ being variable with the quenching temperature is also being tested. Experiments have thus been started to grow single crystals by flux methods at lower temperatures.

Full details of the investigation will be given elsewhere.

This study forms part of a research program supported by *Malmfonden—Swedish Foundation for Scientific Research and Industrial Development*. A grant from *Hierta-Retzius' stipendiefond* is gratefully acknowledged. The use of the electronic computer Facit EDB was made possible by kind permission of the *Computer Division of the National Swedish Rationalization Agency*.

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Received September 2, 1965.