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UNIT CELL DETERMINATION AND THERMAL TRANSFORMATIONS OF NSUTITE

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ABSTRACT

Two unusual specimens of nsutite showing preferred orientation were examined. *x*-ray powder data for massive nsutite and *x*-ray patterns of the "oriented" specimens are correlated. A hexagonal unit cell, $c = 4.43$ Å and $a = 9.65$ Å, accounts for the *x*-ray observations and agrees with the parallel extinction noted optically. *X*-ray diffraction analyses of thermal transformation products of one of the "oriented" specimens are also included.

INTRODUCTION

Nsutite occurs in many localities, but its principal source is Nsuta, Ghana, West Africa. The studies reported by Zwicker *et al.* (1962) and Sorem and Cameron (1960) contain excellent bibliographies of the literature concerning this mineral and its occurrence. Zwicker and co-investigators suggested the name "nsutite" to distinguish it from the various types of synthetically produced manganese oxides. Previously, both the synthetic products and the mineral were designated γ-MnO_2. They assigned to nsutite the formula unit, $Mn_{1-x}^{4+}Mn_x^{2+}O_{2-2x}(OH)_{2x}$ in which $x = 0.06$–0.07.

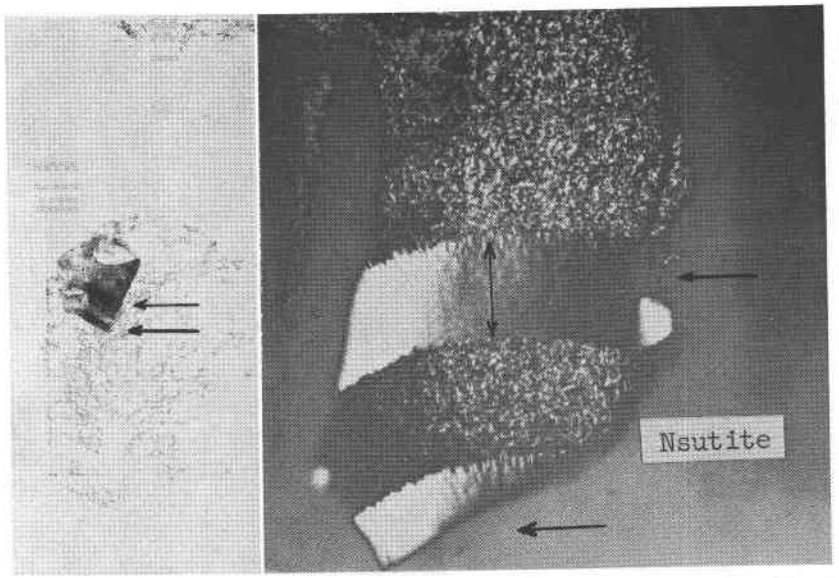
Although nsutite has been recognized as a mineral species since 1940 (Kedesdy *et al.*, 1957), its crystal structure has not been fully described. De Wolff (1959) hypothesized a possible structure based on randomly alternating layers of ramsdellite and pyrolusite to account for the variations in line broadening of the *x*-ray reflections characteristic of the diffraction pattern of gamma-MnO_2. Nye *et al.* (1959) and Kedesdy, *et al.* (1957) suggested that rho- and gamma-type manganese oxides have an orthorhombic unit cell similar to that of ramsdellite, but with the MnO_6^{-2} octahedra rotated approximately 27°. Since nsutite generally occurs as a massive deposit, the crystal structure data and hypotheses reported by other investigators have been derived from powder *x*-ray diffraction data. The two specimens described in this report are unusual, and the only ones with any preferred orientation found in the hundreds of specimens examined.

SAMPLE DESCRIPTION

A massive dark-gray sample with colliform layering was received from Nsuta, Ghana, West Africa. It was identified as nsutite from powder *x*-ray diffraction data. Chemical analyses established that the sample contained 90.46% MnO_2 and 2.51% MnO (calculated by difference from a total manganese content of 59.2%). A combined water or hydroxyl ion

content of 2.5% was determined from a weight loss occurring between 100° C. and 450° C. on a thermal gravimetric balance (heating rate 6° per minute; 1 gram sample). Optical spectrographic analyses showed that a small amount of iron and trace amounts of silicon, sodium and calcium were also present.

Across a small sector of the massive sample were two unusual bands of nsutite with a slightly darker color that could be removed with a sharpened needle in minute rectangular sections under a stereomicroscope



(a) (b)

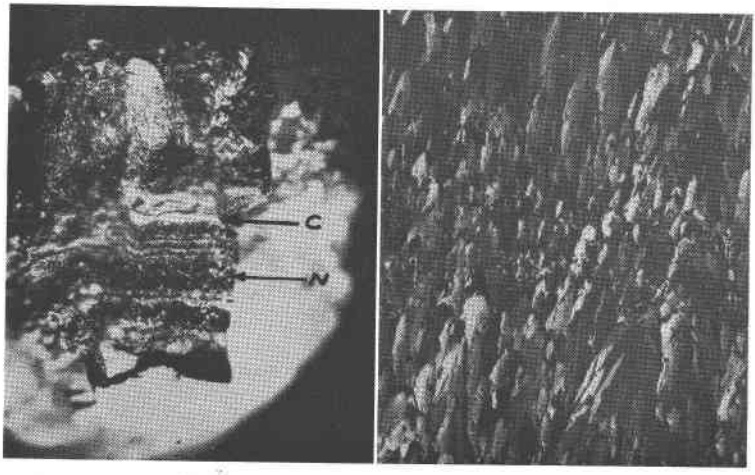
FIG. 1. Photomicrographs showing the oriented and massive nsutite (a) (7×) as-received state, and (b) (50×) after polishing (reflected polarized light). Oriented areas indicated by arrows.

(75×). The area of the sample enclosing the bands was removed, mounted in Lucite and mechanically polished. Figure 1 shows photomicrographs of the sample before and after polishing.

A microscopic examination of the polished section in polarized reflected light (Fig. 1b) established that the material in the bands was comprised of anisotropic acicular particles oriented with their long direction perpendicular to the length of the band. The particles were characterized by parallel extinction.

The second specimen examined also originated in Nsuta, Ghana, West Africa. It was found in a sample of nsutite that had been crushed to 6×8 mesh and was selected because of its fibrous appearance. This specimen

consisted of layers of acicular particles of nsutite oriented with a somewhat common direction separated by thin layers of cryptomelane. The nsutite particles in this specimen also showed parallel extinction. The two minerals, nsutite and cryptomelane, were carefully separated under a stereomicroscope and identified by powder x-ray diffraction. The occurrence of nsutite containing thin layers of cryptomelane has been noted previously by Sorem and Cameron. Photomicrographs of this specimen in the as-received state and after polishing are shown in Fig. 2. A chemical



(a) (b)

FIG. 2. Photomicrographs of nsutite (N) separated by cryptomelane (C) (a) (15×) as-received state, and (b) (150×) layer of acicular particles after polishing (reflected light).

analysis established that the acicular particles of nsutite contained 58.3% manganese. There was not a sufficient quantity of the specimen to determine the MnO_2 content chemically. However, a quantitative optical spectrographic examination showed, in addition to the manganese, calcium and aluminum (less than 1% of each) and trace amounts of silicon, magnesium and copper.

X-RAY DIFFRACTION STUDIES

A diffractometer trace of the massive nsutite surrounding the bands was recorded using MoKα radiation, scanning speed of 1 degree (2θ) per minute, and a scintillation counter detector equipped with a pulse height analyzer. Debye-Scherrer patterns were obtained of the massive nsutite, a carefully removed section of the banded area in the massive nsutite sample, and acicular particles from the fibrous-appearing specimen using FeKα radiation (Straumanis-type camera, 57.3 mm radius). The three

TABLE I. *X*-RAY DIFFRACTION POWDER DATA OF NSUTITE

d (obs)	I (obs)[1]	hkl	d (calc.)	Reflection Characteristics[2]	d (obs) (Data reported by De Wolff, 1959)	hkl
4.43	<1	001	4.43	1		
4.00	9.8	101	3.91	3	3.93	110
2.59	2.1	211	2.57	2	2.624	130
2.42	6.8	220 $4\bar{2}0$	2.41	1	2.430	021
2.33	6.9	301	2.36	2	2.346	111
					2.328	040
2.21	1	002	2.22	1	2.225	200
2.13	4.7	221	2.12	1	2.133	121
2.07	<1	311	2.05	1	2.064	140
1.90	1.4	401	1.89	2	1.863	131
1.635	10.0	222	1.635	1	1.642	221
1.603	4.5	312	1.600	2	1.609	240
1.478	2.3	003	1.478	3	1.497	151
1.424	1.3	600	1.393	1–2	1.426	002
1.367	4.1	340	1.374	3	1.361	061
1.338	1.1	502	1.334	3	1.341	112
1.305	2.0	303	1.304	3	1.303	161 122
1.256	<1	223	1.259	1	1.252	132
1.210	1	403	1.206	1	1.214	042
1.168	<1	441	1.164		1.199	202
1.108	<1	004	1.108		1.161	261
		503	1.107			
1.067	<1	711	1.073		1.066	242
1.060	<1	442	1.058			
1.043	<1	612	1.041			

(1) MoKα radiation.

(2) 1, 2, and 3 are relative values of line broadening, (1) distinct, (3) diffuse, and (2) intermediate.

powder patterns were identical in interplanar spacings, visually estimated reflection characteristics and relative intensities.

A diffractometer chart was also prepared from the massive nsutite specimen mixed with sodium chloride as a calibrating standard. The angles of reflection from the sodium chloride were plotted against the measurements of the corresponding lines to give a calibration chart for the curve. The interplanar spacings and relative integrated intensities are presented in Table I.

It is a well known characteristic of x-ray diffraction patterns of nsutite that some reflections are diffuse whereas others are relatively distinct.

The width of each line on an x-ray diffractometer chart was measured and calculations were made for each reflection as if line broadening resulted from crystallite size. The calculated values were grouped into three categories corresponding to diffuse, distinct, and intermediate-type reflections. These values are included in Table I only to emphasize the differences in line broadening.

A minute rectangularly shaped particle was removed from a band in the massive nsutite sample. The long dimension of the particle was parallel to the direction indicated by an arrow in Fig. 1b. An oscillation pat-

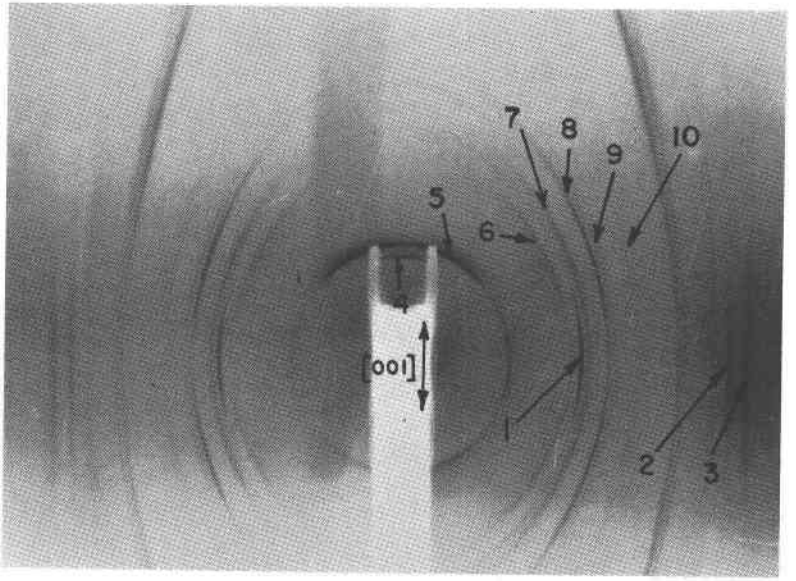


FIG. 3. X-ray pattern of a minute section from banded area shown in Fig. 1. Two-headed arrows correspond to the same direction of the specimen in Figs. 1 and 3.

tern (50° 2θ) of the particle, oriented with its long dimension perpendicular to the x-ray beam and parallel to the axis of the camera (57.3 mm diameter) may be seen in Fig. 3. Several patterns were also taken with the specimen oscillating and stationary at various positions while maintaining the x-ray beam perpendicular to the long dimension of the particle. The same reflections were detected on each of the films. This signifies that the specimen consisted of randomly oriented crystallites around a nearly common axis. The identity distance was calculated as 4.43 Å and was designated as the [001] direction. The reflections, d = 2.42 Å, 1.42 Å, and 1.36 Å, have their maximum intensities on the zero layer line. These reflections are designated by arrows and the numbers 1, 2, and 3, respec-

tively, on Fig. 3. The reflections d = 4.43 Å, 4.00 Å, 2.59 Å, 2.33 Å, 2.13 Å, 2.07 Å, and 1.90 Å occur on the first layer line. They are indicated by the numbers 4 through 10, respectively. Although it is difficult to detect the reflections, d = 4.43 (No. 4), d = 2.07 (No. 9), and d = 1.90 Å (No. 10) on the reproduction, they were easily seen on the original film.

The reflection, d = 4.43 Å, occurs on a vector perpendicular to the zero layer line. This indicates that the [001] direction is perpendicular to the [100] and [010] directions. It was found that a hexagonal unit cell with the dimensions $a = 9.65$ Å and $c = 4.43$ Å could account for the observed data. The calculated interplanar spacings are included in Table I. The calculated density is 4.86 for a unit cell containing 12 formula units of Mn_{1-x}^{+4} Mn_x^{+2} O_{2-2x} $(OH)_{2x}$ ($x = 0.06$). Although the density value reported for nsutite from Ghana is 4.55, the density was found to vary from 4.24 to 4.67 and to depend on the origin of the mineral (Zwicker *et al.*, 1962).

A small acicular particle was removed from the fibrous-appearing specimen and mounted with its long direction perpendicular to the *x*-ray beam (parallel to the axis of the camera). It was concluded from a comparison of patterns obtained from this specimen held stationary and oscillated that this specimen also consisted of randomly oriented crystallites around a nearly common direction.

Figure 4 shows the *x*-ray pattern obtained from the specimen when stationary. The identity distance was measured as approximately 9.7 Å. The different growth directions for the two specimens were not considered unusual, since nsutite generally forms by replacement (Sorem and Cameron, 1960) and minerals formed by this process frequently take the growth habit of the original host mineral. In fact, pseudomorphs are good evidence of a replacement type of formation (Edwards, 1954).

The long direction of the acicular particle was parallel to the $[1\bar{1}0]$ direction. The interplanar spacings, 4.43 Å (001), 2.42 Å (220), 2.13 Å (221), 1.635 Å (222), 4.00 Å (101), and 2.59 Å (211) are indicated by the numbers 1 through 6, respectively, on Fig. 4. The reflection, d = 4.43 Å, is also very faint on this photograph. A small sector of the zero layer line, reproduced to emphasize the relative positions of the reflections, d = 4.43 Å and d = 4.00 A, is included in Fig. 4. A comparison of the Debye-Scherrer pattern of the massive nsutite surrounding the banded area and the zero layer lines of the patterns shown in Figs. 3 and 4 is presented in Fig. 5.

Byström (1949) assigned an orthorhombic unit cell to synthetic gamma-MnO_2 ($a = 4.43$ Å, $b = 9.36$ Å, $c = 2.85$ Å) and considered the structure related to pyrolusite and ramsdellite. De Wolff (1959) examined three samples of gamma-MnO_2 and assigned a unit cell similar to that of Byström's. He considered the unit cell to vary ($a = 4.45$ Å to 4.489 Å,

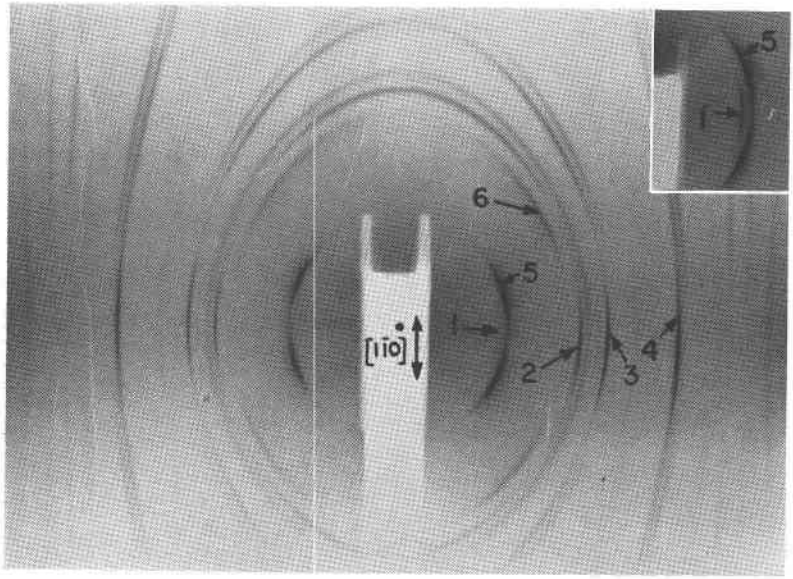


FIG. 4. *X*-ray pattern of an acicular particle from the layer of nsutite shown in Fig. 2b. A sector of the zero layer line is shown in the upper right corner to emphasize the relative positions of the reflections, 4.43 Å and 4.00 Å.

$b = 9.305$ Å to 9.31 Å, $c = 2.850$ to 2.848 Å). Kedesdy *et al.* (1957) reported a chain structure of MnO_6^{-4} octahedra for the orthorhombic unit cell ($a = 4.418$ Å, $b = 9.510$ Å, $c = 2.811$ Å).

The interplanar spacings given by Byström (1949) do not account for all the reflections detected for nsutite. Although De Wolff (1959) does not state whether his specimens were synthetically produced or naturally occurring, the interplanar spacings reported are similar to those of the mineral. The interplanar spacings reported in Table I bear close resemblance to those reported for "Nsuta-type 1.64" (Sorem and Cameron, 1960) and for nsutite (Zwicker *et al.*, 1962).

The (h) indices for the reflections reported by De Wolff (1959) (see Table I) for the direction having the dimension of 4.43 Å are in close agreement with the (1) indices derived from the *x*-ray pattern shown in Fig. 3. However, his (hkl) values could not be correlated with a common or nearly common crystallographic direction that would account for the *x*-ray pattern shown in Fig. 4.

THERMAL TRANSFORMATIONS

Acicular particles from the fibrous-appearing specimen were heated at various temperatures for different times. After heating, *x*-ray patterns

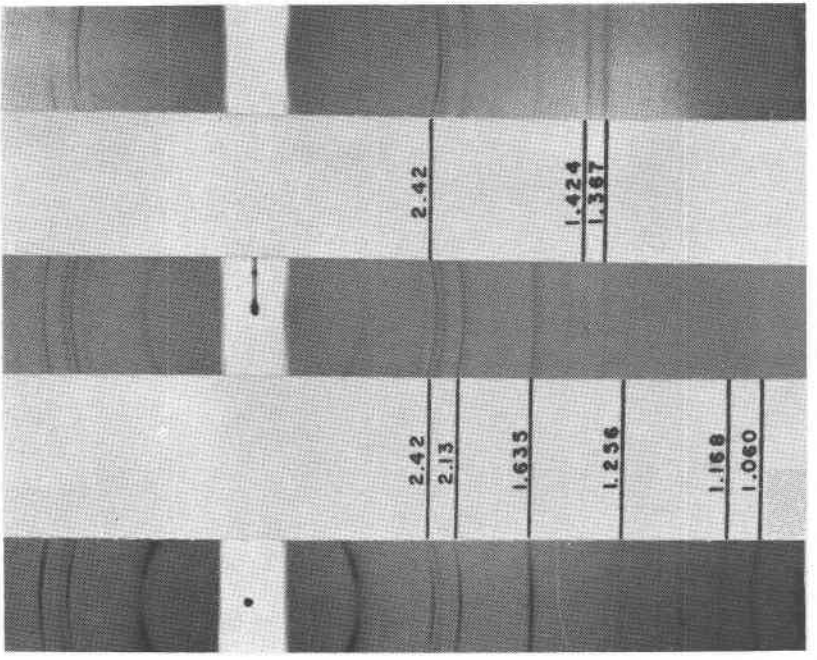


FIG. 5. Comparison of (a) zero layer line of nsutite oriented along the [001], (b) Debye-Scherrer pattern of massive nsutite, and (c) zero layer line of nsutite oriented along the [1$\bar{1}$0].

were taken of the specimens mounted in a 57.3-mm diameter camera and held stationary with their long dimension ([1$\bar{1}$0] of the original specimen) perpendicular to the x-ray beam (FeKα).

The x-ray pattern of a specimen heated at 200° C. for four hours was the same as the pattern of the original specimen (Fig. 4). After a heat treatment at 300° C. for 21 hours, the intensities of the reflections, d = 4.00 Å, 1.603 Å, and 1.478 Å, were decreased appreciably. The reflections, d = 2.59 Å and 2.33 Å, were not detected. The x-ray pattern showed preferred orientation and the reflections d = 2.42 Å, 2.13 Å, and 1.603 Å were on the zero layer line.

The reflection, d = 4.00 Å, was not detected after heating a specimen at 400° C. for 21 hours (Fig. 6). The interplanar spacings recorded were identical with those characteristic of pyrolusite; however, the reflection d = 3.1 Å was diffuse. This reflection, emphasized by an arrow in Fig. 6, showed a definite preferred orientation. The other reflections were distinct and almost continuous.

The only phase detected on an x-ray pattern of a specimen heated at 600° C. for 17 hours was Mn_2O_3, with a small degree of preferred orienta-

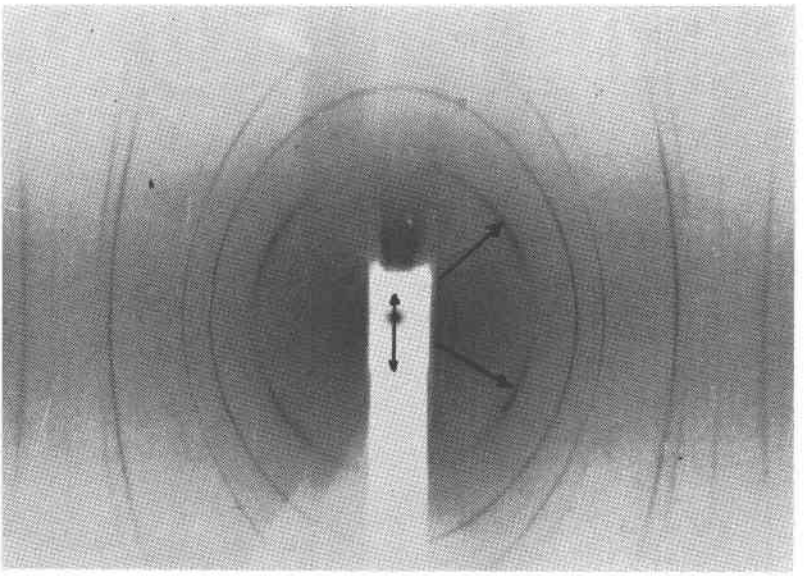


FIG. 6. X-ray pattern of a nsutite oriented along the [1$\bar{1}$0] and heated at 400°C. for 21 hours. Diffuse reflections having an interplanar spacing of d = 3.1 Å are indicated.

tion along its [100] axis (originally [1$\bar{1}$0]). The sample of nsutite heated at 1000° C. for 2 hours showed no orientation and was identified as Mn_3O_4 (tetragonal).

SUMMARY

Two unusual specimens of the manganese oxide mineral, nsutite, were examined. Each specimen was comprised of crystallites randomly oriented around a nearly common crystallographic axis. Particles from both specimens showed parallel extinction in polarized reflected light. A hexagonal unit cell ($a = 9.65$ Å and $c = 4.43$ Å) is assigned to the mineral. The observed interplanar spacings from x-ray powder data are compared to calculated values. The calculated density is 4.86 for 12 formula units of $Mn_{1-4}^{4+}Mn_x^{2+}O_{2-2x}(OH)_{2x}$ where $x = 0.06$.

The thermal transformation products of one of the oriented specimens were examined by x-ray diffraction. It was found that (1) the diffuse x-ray reflections characteristic of nsutite are the first to disappear, (2) a material having one diffuse discontinuous reflection and the remaining reflections distinct and continuous is produced by heating at 400° C. and (3) slightly oriented Mn_2O_3 results from heating at 600° C.

References

Byström, A. M. (1949) The crystal structure of ramsdellite, an orthorhombic modification of MnO_2. *Acta Chem. Scand.* **3,** 163–173.

De Wolff, P. M. (1959) Interpretation of some gamma-MnO_2 diffraction patterns. *Acta Cryst.* **12,** 341–345.

Edwards, A. B. (1954) *Textures of the Ore Minerals and Their Significance.* Australasian Inst. Mining Metall. (Inc.), 115–123.

Kedesdy, H., G. Katz and S. B. Levin (1957) Structural relationship between ramsdellite and some synthetic manganese oxides. *Acta Cryst.* **10,** 780–781.

Nye, W. F., S. B. Levin and H. H. Kedesdy (1959) Structure and morphology of manganese dioxide. *Proc. 13th Ann. Power Sources Conf.*, 125–129.

Sorem, R. K. and E. N. Cameron (1960) Manganese oxides and associated minerals of the Nsuta manganese deposits, Ghana, West Africa. *Econ. Geol.* **55,** 278–310.

Zwicker, W. K., W. O. J. Groeneveld Meijer and H. W. Jaffe (1962) Nsutite—A widespread manganese oxide mineral. *Am. Mineral.* **47,** 246–266.

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