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Crystal Structures and Expansion Anomalies of MnO, MnS, FeO, Fe₃O₄ Between 100°K and 200°K*

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(1) Determinations have been made of structure type and lattice constants of MnO, MnS, FeO and Fe₃O₄ at temperatures near those at which these substances show specific heat anomalies. (2) No major structure changes were apparent in the x-ray patterns. All structures are cubic at all investigated temperatures. Lattice constant

data indicate similarity in the abnormal expansion behavior of MnS and FeO and of MnO and Fe₃O₄. (3) The specific heat and expansion anomalies are probably due to electron transitions within certain atoms in the crystal lattice and may be analogous to the behavior of metallic iron at 765°C, or of quartz at 575°C.

INTRODUCTION

ACCORDING to results of recent experiments carried out by Millar¹ and Anderson² at the Pacific Experiment Station of the Bureau of Mines, MnO, FeO, Fe₃O₄ and MnS show anomalies in their specific heat curves. Each curve shows a cusp or hump superimposed upon the normal ascending trend. The plots of heat capacity *versus* temperature for these four compounds are reproduced in Figs. 2, 3, 4 and 5. For exact numerical data reference should be made to the original publication.

Whenever a transition in state occurs, there results an abnormal absorption or evolution of energy. Consequently, the relation between heat capacities and temperature is quite helpful in locating such transitions. The change from one structure to another is usually accompanied by a heat absorption or evolution over a relatively short temperature range.

Experiments have been reported which show that the abnormal absorption of energy is not always accompanied by change in crystal struc-

ture. Simon³ discovered anomalous specific heat behavior in ammonium chloride at some point between 223° and 243°K. Investigation of the crystal structure at these low temperatures by Simon and v. Simson^{4, 5} shows anomalous behavior at 242.3°K for ammonium fluoride, at 242.6°K in the case of ammonium chloride, at 235°K in the case of ammonium bromide and at 230.5°K in the case of ammonium iodide.

Klinkhardt⁶ in his work on specific heat of iron found two outstanding abnormalities in the specific heat curve. One of these abnormalities, occurring in the neighborhood of 906°C, represents a sharp drop in the specific heat curve and is explained by Westgren and Lind's⁷ work showing a change from the body-centered cubic lattice of the alpha iron to the face-centered cubic lattice of the gamma iron. The other specific heat anomaly which takes place over a considerable temperature range and which reaches a maximum at 765°C, cannot be accounted for on the basis of crystal structure change. However, it is interesting to note that the peak of this curve occurs at the same point at which the iron loses its ferromagnetic properties.⁸

* Presented by Nelson W. Taylor before the Division of Physical and Inorganic Chemistry at the Washington meeting of the American Chemical Society, 1933.

† Submitted in partial fulfillment of the requirements for the degree of Master of Science, June 1933.

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¹ R. Millar, *J. Am. Chem. Soc.* **50**, 1875-83 (1928); **51**, 215-22 (1929).

² C. T. Anderson, *J. Am. Chem. Soc.* **53**, 476-83 (1931).

³ F. Simon, *Ann. d. Physik* **68**, 241 (1922).

⁴ F. Simon and v. Simson, *Naturwiss.* **38**, 880 (1926).

⁵ F. Simon and v. Simson, *Zeits. f. physik. Chemie* **129**, 339 (1927).

⁶ H. Klinkhardt, *Ann. d. Physik* **84**, 167-200 (1927).

⁷ A. Westgren and A. Lind, *Zeits. f. physik. Chemie* **98**, 181 (1921).

⁸ Weiss, *J. de Physique* **7**, 249 (1908).

APPARATUS

The source of x-rays for all pictures taken in this experiment is a Siegbahn metal x-ray tube with an iron target.⁹ The camera is one designed by Taylor.¹⁰ Slight modifications were made to reduce thermal capacity. The specimen is mounted on a wire passing vertically through the camera at its center. The film is placed in a cylindrical envelope and fastened securely about the outer side. For the purpose of thermal insulation, the camera is packed in cotton in a wooden box lined on the inside with tin foil. There are three small openings in the box, one on the side for the slit system of the camera, one for the thermocouple and ground leads and the final one on top for a gas inlet. The outer end of the slit system is flush with the outside edge of the box to permit as great insulation as possible.

TEMPERATURE MEASUREMENTS

A copper-advance thermocouple was constructed from No. 30 insulated copper wire and No. 30 insulated "advance" wire. Three advance wires and one copper wire lead to the variable junction, the wires at these points being soldered by means of tin solder.

The potentials generated by this thermocouple were measured by means of a Leeds and Northrup Type K Potentiometer No. 169339 with lower-limit voltage readings at 0.000001 volt. The potentiometer was standardized by means of a Weston Standard Cell having a voltage of 1.0188. The same standard cell was used throughout all the experiments.

Calibration of the thermocouple was carried out according to the method described by Adams.¹¹ This method involves the determination of a correction curve showing deviations of e.m.f. from a set of standard values of e.m.f. as given by a general equation. The deviations are obtained by observing the potential generated when one junction is in ice water (0°C or 273°K) and the other junction is in a definite and accurate temperature bath. The standard values for the

low temperature calibration were obtained from Volume 1, page 57 of the *International Critical Tables*. The fixed temperature points used were (1) the boiling point of O₂,

$$t = (-183.00 + 0.0126(p - 760) - 0.0000065(p - 760)^2)$$

where p is the atmospheric pressure in millimeters and t is temperature in degrees centigrade; (2) the melting point of ethyl acetate (-83.6°C); (3) the melting point of mercury (-38.87°C) and (4) the melting point of carbon tetrachloride (-22.9°C). The thermocouple was checked against a calibrated Bureau of Mines platinum resistance thermometer (Wheatstone Bridge, Leeds and Northrup No. 88131) and satisfactory agreement was obtained. The sensitivity of the apparatus used makes thermocouple readings accurate to $\pm 0.1^\circ\text{C}$.

GENERAL PROCEDURE

The general set-up is shown in Fig. 1. *A* and *B* are two 500 cc wide mouth bottles containing solid KOH for removal of CO₂, *C* is an 800 cc wide mouth bottle containing anhydrous calcium chloride for removal of H₂O, *D* is a 1/2 liter

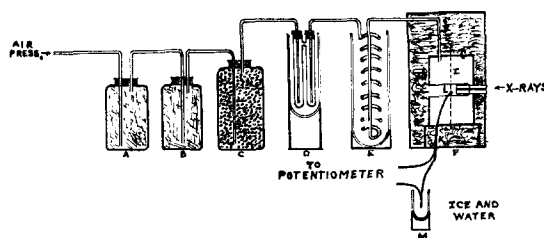


FIG. 1. Low temperature x-ray camera.

Dewar in which is placed a set of 1" × 8" liquid air traps arranged in series, *E* is a 1-liter Dewar containing a meter of 6 mm copper tubing in the shape of a coil, *F* is a wooden box lined with tin foil. Inside this box, packed in cotton, is the camera *G*. *K* represents the thermocouple leads to the variable junction which is fastened to the wire specimen holder *I*, immediately below the point at which the x-rays coming through the slit *H* strike the specimen *L*. *M* is a 250 cc Dewar which contains the ice and water mixture for cold junction. The specimen was ground to powder in

⁹ Siegbahn, *Spectroscopy of X-rays*, Oxford University Press (1925).

¹⁰ N. W. Taylor, *Rev. Sci. Inst.* **2**, 751-55 (1931).

¹¹ Adams, *J. Am. Chem. Soc.* **36**, 65 (1914).

an agate mortar and placed on the wire specimen holder by means of collodion. Wood's metal was used in connecting the thermocouple to the specimen holder, since its melting point is so low that it can be applied easily and also will not affect the solder used in making copper-advance connections. A relatively large amount of Wood's metal was used so as to make a thermal reservoir near the specimen.

When the film is in position the only openings remaining in the camera are the tube on the upper side for gas inlet, the slit for x-ray entrance at the side and the tube at the bottom for entrance of thermocouple leads. Constant temperature was obtained by streaming cooled gas through the camera at such a rate as to counteract exactly heat increase from without.

The thermal capacity of the camera is relatively large so that small variations in the rate of flow of the gas will not be noticeable. However, during the period of an exposure, from two to three hours, air pressure and room temperature changes may require that slight adjustments be made in the rate of flow. Temperature deviations from the constant value desired are considered as being confined to a range of $\pm 0.5^\circ\text{C}$.

Pictures of each of the compounds were taken at various temperatures throughout the range. Each is listed in a tabulated form below. In general, a picture of each substance was taken (1) at room temperature, (2) at the temperature corresponding to the peak of the anomaly in the specific heat curve and (3) and (4) at temperatures above and below the anomaly.

MATERIALS

In these experiments we are dealing with the same material as used in the specific heat determinations. We are grateful to Dr. Charles G. Maier of the Bureau of Mines Pacific Experiment Station, Berkeley, California who has kindly supplied the compounds used. Complete details as to the preparation of these compounds are given in the reports on specific heat data.

MEASUREMENTS

The films were developed and measurements were made on negatives. The distances between outside edges of corresponding lines were meas-

ured to an accuracy of 0.1 mm. Under the conditions of the experiment it is impossible to give the exact dimensions of the camera. The temperature measurements made are those of the central wire and not of the camera and hence the radius of the camera cannot be assumed. It is, therefore, necessary to use some standard whose lattice constant is known so that the film may be calibrated. In relation to the compounds studied, the standard chosen must not only give lines which do not coincide with those of the compound but must also give enough lines throughout the range of the film so that calibration will be complete. No measurements of lattice constants of elements for low temperatures are recorded in the literature but, assuming that coefficient-of-expansion data are applicable to the side of a unit cell, we can calculate, on the basis of lattice constant at room temperature and coefficient of expansion data at low temperatures, the value of the lattice constant of the standard at the low temperatures.

Mo was chosen as a standard for the compounds MnS, FeO and Fe_3O_4 . In the case of MnO, platinum wire was used, since the diffraction lines of MnO and Mo are coincident to the extent that they cannot be distinguished on the film.

The coefficient of linear expansion of Mo wire is given by Schad and Hidnert¹² as

$$L_t = L_0(1 + 5.15t \times 10^{-6} + 0.00570t^2 \times 10^{-6}),$$

t being the temperature in degrees centigrade. This value agrees very well with results presented by Disch.¹³

Coefficient-of-expansion data for platinum wire given by Dorsey were plotted and the average value over the range in question was obtained from the graph.

Approximate values of the angle of reflection, 2θ , and of $\sin^2 \theta$, were obtained by assuming 57.85 mm as the effective diameter of the camera. Then by using the calculated lattice constants for various temperatures, the true values of $\sin^2 \theta$ for the reflections from the different planes in the standard were calculated from Bragg's equation.

$$n\lambda = 2d \sin \theta,$$

¹² Schad and Hidnert, *Phys. Rev.* **13**, 148 (1919).

¹³ J. Disch, *Zeits. f. Physik* **5**, 173 (1921).

TABLE I. Data: *MnO series*: III. MnO on Pt wire at 115°K. Film 266: Fe rad., 30 k.v. 15 m.a., 2 hr.: Lattice Constant $Pt = 3.904\text{\AA}$, $s = 0.06\text{ cm}$.

Relative intensity	$2d-s$ (cm)	2θ	Observed $\sin^2 \theta$	Calculated $\sin^2 \theta$ for Pt lines	Corrected $\sin^2 \theta$	Indices	$\sin^2 \theta$
st.	12.34	122.21	0.7665		0.7674	(400)	(16) (0.04795)
m.	11.92	118.06	.7352	0.7362 (222)			
st.	11.10	109.93	.6704	.6748 (211)			
st.	9.89	97.95	.5691		.5750	(222)	(12) (.04791)
st.	9.32	92.31	.5209		.5275	(311)	(11) (.04795)
m.	8.90	88.15	.4838	.4908 (220)			
v. s.	7.66	75.86	.3779		.3836	(220)	(8) (.04795)
m.	5.94	58.83	.2412	.2454 (200)			
st.	5.20	51.50	.1887		.1918	(200)	(4) (.04795)
v. st.	4.47	44.37	.1419		.1439	(111)	(3) (.04796)

$\sin^2 \theta = 0.04795 (h^2 + k^2 + l^2) \cdots \text{FeK}\alpha$
 $a_{\text{MnO}} = (1.934)^2 / (4) (0.04795) = 4.416\text{\AA}$

which, in case of a cubic lattice, may be written

$$\sin^2 \theta = (\lambda^2 / 4a^2) (h^2 + k^2 + l^2).$$

The difference between the true and the observed values as plotted on a graph showing the relation between observed $\sin^2 \theta$ and correction (difference between true and observed $\sin^2 \theta$). By making use of these correction curves, the correct values of $\sin^2 \theta$ for all lines were obtained. Since the lines of the standard cover the range of the whole film, these correction curves also eliminate errors that may be due to the film itself, such as warping. The results are listed in tables showing the identification of lines with their respective crystal planes. Although lines due to Fe beta-rays were identified, only values resulting from lines due to Fe alpha-rays were used in calculating the lattice constants. The lattice constants are accurate to $\pm 0.002\text{\AA}$.

A typical set of data is presented in Table I, but on account of space similar data for the seventeen studied cases will not be given.

The lattice constants of the several substances are summarized in Table II.

The variations of the lattice constants with

TABLE II. Lattice constants in Angstrom units at low temperatures.

MnO	°K	Fe ₃ O ₄	°K	MnS	°K	FeO	°K
4.436	299	8.363	299	5.210	299	4.290	299
4.409	160	8.357	160	5.204	160	4.286	200
4.416	115	8.363	114	5.204	143	4.284	186
4.419	104	8.363	104	5.197	138	4.283	160
				5.192	130		

temperature are clearly anomalous. Note the minimum in the case of MnO and of Fe₃O₄ at 160°K. Refer to Figs. 2, 3, 4, and 5 for a plot of the lattice constant data. It should be stated that no change in crystal structure type appeared in the x-ray patterns. The only changes appear to be the irregularities in the expansion behavior.

DISCUSSION

Okamura¹⁴ has carried out dilatometric measurements on magnetite. According to the graph given in his report Fe₃O₄ expands with decrease in temperature from 173°K to 73°K. In the same report, it is stated that x-ray pictures by Nishiyama revealed no change in structure. However, no description of the method used and no values for calculation are given. Two other physical phenomena of interest that occur at the transition point are: (1) an abnormally great increase of specific resistance with decrease in temperature and (2) a sudden fall in intensity of magnetization after having gradually increased with decreasing temperature.

Quoting from Okamura's work:

So far as the relative position of iron atoms in magnetite is concerned, alpha and beta magnetite have no noticeable difference. It is, however, to be noted that it is difficult to find the position of oxygen atoms in the iron lattice by Debye-Scherrer's method of x-ray analysis. . . . Thus the transformation of magnetite alpha \rightleftharpoons beta is probably due to a small displacement of oxygen atoms in the magnetite.

¹⁴ T. Okamura, Science Reports Tohoku Imp. Univ., First series 21, 2, 231-241 (1932).

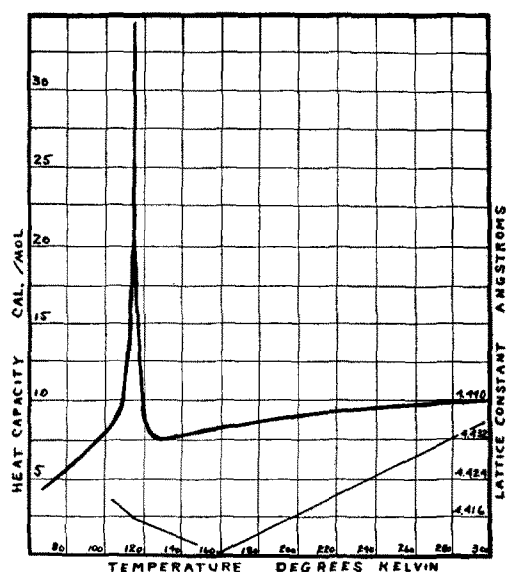


FIG. 2. MnO: Relation between heat capacity, lattice constant and temperature.

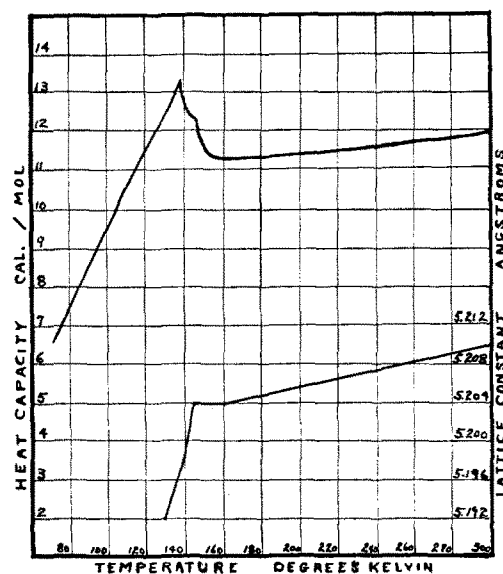


Fig. 4. MnS: Relation between heat capacity, lattice constant and temperature.

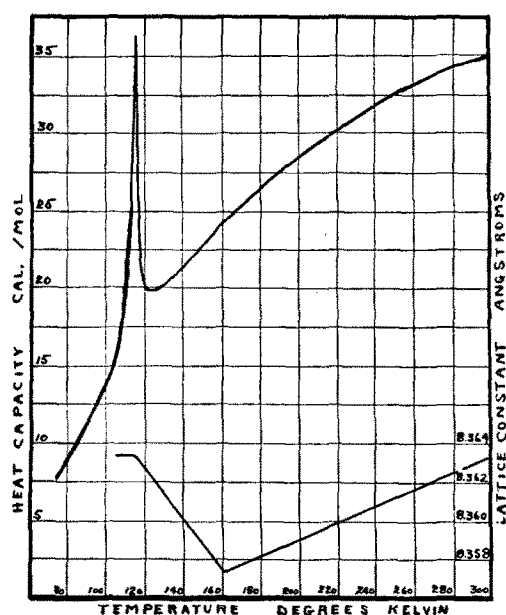
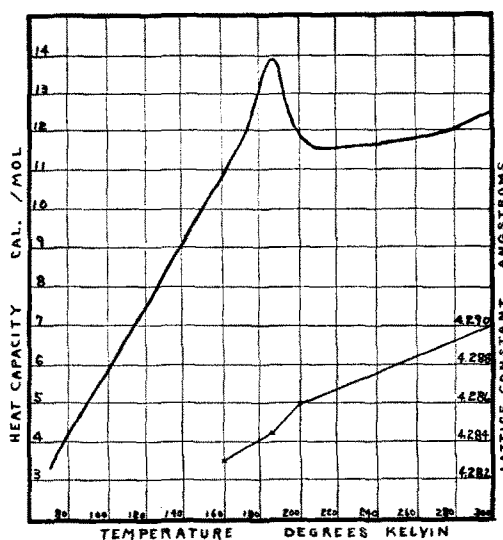
FIG. 3. Fe_3O_4 : Relation between heat capacity, lattice constant and temperature.

FIG. 5. FeO: Relation between heat capacity, lattice constant and temperature.

Hence, in order to know the nature of this transformation it is necessary to compare the Laue spots of alpha and beta magnetites. So far as any change of physical properties at the transformation temperature is concerned, magnetite shows a similar behavior to that of quartz. That is, quartz (SiO_2) has an allotropic transformation at 573° ; this change can be traced by those of thermal expansion, specific heat, electrical conductivity and magnetic susceptibility. Rinne found

by means of x-ray analysis that the transformation of quartz alpha \rightarrow beta is due to a small displacement of oxygen atoms. Thus in all probability the transformation in magnetite is similar to that in quartz. It is very interesting to note that the transformation in magnetite and in quartz which consists only of the small change of distribution of the oxygen atoms in the iron lattice affects the electrical and magnetical properties to a considerable degree. This marked

effect is probably caused by some change in the valence electron in the atoms, which may reasonably take place as the result of small displacement of atoms in that lattice. Thus the transformation of a substance may consist of three changes, that is,

- (1) change of lattice,
- (2) change of state of electrons in atoms,
- (3) change of orientation of atoms.

In the case of magnetite and quartz, change (1) is probably small but (2) and (3) are considerable.

By dilatometric measurements carried out by Simon and Bergmann¹⁵ it is shown that ammonium chloride increases in volume at the transition point, while ammonium bromide and ammonium dihydrogen phosphate gradually contract during the transition interval. Kracek¹⁶ noted an abnormal expansion of sodium nitrate.

Investigations by Southard, Milner and Hendricks¹⁷ on normal amyl ammonium chloride indicate a similar behavior.

On the basis of a wave-mechanical treatment, Pauling¹⁸ shows how many gradual transitions from an oscillatory state to one of rotation can arise in solids where the moments of inertia are small and the intermolecular forces are also small. Such transitions usually are "foreshadowed on the low temperature side by an abnormal increase in heat capacity."

S. B. Hendricks, E. Posnjak and F. C. Kracek have investigated ammonium nitrate¹⁹ and explain some of their results on the basis of rotation of nitrate ions. The abnormalities in ammonium halides to which reference was made at the beginning of this paper are explained on the basis of rotation of ammonium ion.

On the other hand, in solids having strong intermolecular ionic or atomic forces such transitions from oscillation to rotation are less likely. In view of the fact that MnO, FeO, MnS and Fe₃O₄ are all rather polar compounds of high melting point, hardness, etc., they would seem to fall into this latter class. We must therefore look

for another interpretation of their anomalous specific heat and expansion behavior.

As far as behavior of the specific heat curve is concerned, Fe at 765°C is quite analogous to the compounds we have studied. Since this abnormality was explained by magnetic changes we may expect them in our compounds. Okamura's work bears out this argument. Of interest in this connection is the fact that CuO shows abnormalities in its specific heat behavior while Cu₂O does not.¹ Cu₂O is diamagnetic whereas CuO is paramagnetic. All of the compounds which we have studied are paramagnetic. J. H. Van Vleck²⁰ states:

Even in paramagnetic bodies some anomalies in specific heat curves should be expected. There is a considerable amount of spin coupling between paramagnetic ions due to the Heisenberg exchange effect, provided the material is one of fairly high magnetic concentration, e.g., MnS, MnO, Fe₃O₄. This is presumably the cause of anomalies in MnS and CuO. It might be described as a potentially ferromagnetic body above the Curie point. It should alter the specific heat but it is not at all clear that it should give a cusp in the curve. In fact, the conventional theory gives an anomaly only at the Curie point with no change in specific heat above.

The specific heat curves of MnO and Fe₂O₃ show striking similarity. The abnormality in each case is very great and is confined to about 20° and the peak is at practically the same temperature (115°K for MnO and 114°K for Fe₃O₄). Above the abnormal range and up to 300°K, the *C_p* curve is a continuation of the initial stage and also is concave to the temperature axis in each case. Curiously enough both substances show contraction as the temperature rises through the abnormal range from 104° to 160°, followed by expansion at higher temperatures. It may be of interest to bear in mind that Fe⁺⁺⁺ ion in magnetite has essentially the same electron structure as Mn⁺⁺ in MnO. In the case of MnS, the bond is probably not of a simple ionic type because of polarization of the sulfide ion.

The specific heat curves of MnS and FeO are similar to one another in shape but different from MnO and Fe₃O₄. They both have relatively large expansion through the abnormal interval fol-

¹⁵ F. Simon and R. Bergmann, *Zeits. f. physik. Chemie* **B8**, 255 (1930).

¹⁶ F. C. Kracek, *J. Am. Chem. Soc.* **53**, 2609-24 (1931).

¹⁷ Southard, Milner and S. B. Hendricks, *J. Chem. Phys.* **1**, 95-102 (1933).

¹⁸ L. Pauling, *Phys. Rev.* **36**, 430 (1930).

¹⁹ S. B. Hendricks, E. Posnjak and F. C. Kracek, *J. Am. Chem. Soc.* **54**, 2766-86 (1932).

²⁰ J. H. Van Vleck, private communication.

lowed by smaller expansions at higher temperatures.

This is seen from the following data:

Temperature range	160–200°K	200–299°K
Coefficient of expansion of FeO	1.75×10^{-5}	0.94×10^{-5}
Temperature range	130–160°K	160–299°K
Coefficient of expansion of MnS	7.7×10^{-5}	0.83×10^{-5}

It is difficult to say that there is a real difference in the behavior of MnS and FeO as compared with MnO and Fe_3O_4 but the data would seem to indicate it. Magnetic susceptibility measurements over the abnormal temperature range of each of the substances may bring out more clearly any difference.