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Alpha Ferric Oxide: Low Temperature Heat
Capacity and Thermodynamic Functions¹

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The heat capacity of synthetic α -Fe₂O₃ was determined from 5 to 350°K. No heat-capacity anomaly was observed at the magnetic transition about 250°K. Thermodynamic functions have been calculated and the values of C_p , S° , $H^\circ - H_0^\circ$, and $-(F^\circ - H_0^\circ)/T$ at 298.15°K. are: 24.80 cal. deg.⁻¹ mole⁻¹, 20.889 cal. deg.⁻¹ mole⁻¹, 3718.9 cal. mole⁻¹, and 8.416 cal. deg.⁻¹ mole⁻¹, respectively.

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The heat capacity of alpha ferric oxide has previously been measured³ over only four narrow regions between 90 and

(3) G. S. Parks and K. K. Kelley, J. Phys. Chem., 30, 47 (1926).

290°K. and it was considered of interest to extend the measurements to lower temperatures and obtain accurate thermodynamic data for this compound. Moreover, $\alpha\text{-Fe}_2\text{O}_3$ is a substance of rather complex magnetic properties,⁴ having a weak ferromagnetism,

(4) L. Néel, Ann. phys., 4, 249 (1949).

which disappears below about 260°K., superimposed on its anti-ferromagnetism.

In the study by Parks and Kelley³ two different samples were used, one consisting of large crystals of specular hematite, the other of a finely divided powder prepared from iron oxalate (Kahlbaum). The heat capacity of the synthetic sample was considerably higher (3.8% at 90°K., 2.4% at 275°K.) than of the mineral, which was explained on the basis of its somewhat amorphous state, as inferred from x-ray powder photographs. The lower values of the specular hematite were adopted, and the resulting entropy at 298°K. found to be 21.5 ± 0.5 e.u. Apart from these data a series of enthalpy measurements on a synthetic

sample have been made⁵ over three regions in the range 81 to

(5) A. S. Russell, Physik. Z., 13, 59 (1912).

317°K.

Neutron diffraction⁶ work on $\alpha\text{-Fe}_2\text{O}_3$ in the range 80 to

(6) C. G. Shull, W. A. Strauser, and E. O. Wollan, Phys. Rev., 83, 333 (1951).

1000°K. confirmed earlier x-ray data^{7,8,9} leading to a rhombo-

(7) L. Pauling and S. B. Hendricks, J. Am. Chem. Soc., 47, 781 (1925).

(8) V. Montoro, Gazz. Chim. Ital., 70, 145 (1940).

(9) N. V. Belov and V. I. Mokeeva, Trudy Dok. Akad. Nauk SSSR, 57, 819 (1947).

hedral unit cell containing two formula units, with the oxygen atoms forming a slightly distorted close packing and 2/3 of the octahedral interstices filled by iron atoms. The structure consists of sheets of iron atoms parallel to the (111) plane, and sheets of oxygen atoms in between. In concordance with the view expressed by Néel⁴ about the magnetic properties of $\alpha\text{-Fe}_2\text{O}_3$ being caused by superposition of the intrinsic antiferromagnetism by a feeble ferromagnetism due to "impurity", the neutron diffraction data indicated the existence of an antiferromagnetic structure. All four iron atoms in the unit cell are located on

the space diagonal. The neutron diffraction data suggests that they are non-equivalent and have relative spin orientation (+--+). At room temperature the moments seem to be parallel to the (111) plane and directed towards one of the three nearest neighbors, while at lower temperatures they are oriented normal to the (111) plane, or in other words, in the [111] direction.

This change in the direction of the moments causes the parasitic ferro- or ferrimagnetism to disappear below about 250°K. according to the magnetic-susceptibility data by Morin¹⁰

(10) F. J. Morin, Phys. Rev., 78, 819 (1950).

and in the range 240 to 190°K. according to the magnetization data by Guillaud¹¹ on pure synthetic samples. The latter author

(11) C. Guillaud, J. phys. rad., 12, 489 (1951).

found that the transition temperature decreased with increasing strength of the magnetic field and also a discontinuity in the resistivity of $\alpha\text{-Fe}_2\text{O}_3$ and rather pronounced changes in the expansion coefficient in the range of the anomaly. No latent heat was detected, although the presence of a second-order transition could not be excluded. The transition was studied further by Néel and Pauthenet¹² and interpreted by Néel¹³ by

(12) L. Néel and R. Pauthenet, Compt. rend., 234, 2172 (1952).

(13) L. Néel, Revs. Mod. Phys., 25, 58 (1953).

supposing that the ferromagnetism consisted of an isotropic and an anisotropic part. The anisotropic part is only observed above 260°K., i.e., when the magnetic moment is in the (111) plane. Studies of the thermomagnetic properties¹⁴ of two natural

(14) H. Bizette, R. Chevallier, and B. Tsai, Compt. rend., 236, 2043 (1953).

hematite crystals showed in contrast to those measured by Néel and Pauthenet¹² only the anisotropic part of the ferromagnetism at room temperature. On cooling, this ferromagnetism in the (111) plane gradually disappeared from 253 to 173°K. The low-temperature susceptibility values found were in accord with those reported by Morin¹⁰ and Guillaud.¹¹ Properties of the isotropic and anisotropic ferromagnetism in hematite were measured in the range 200 to 300°K. by Haigh¹⁵ and a cyclic

(15) G. Haigh, Phil. Mag., 2, 877 (1957).

hysteresis effect studied in detail.

Magnetic-resonance measurements on $\alpha\text{-Fe}_2\text{O}_3$ confirm the presence of a highly anisotropic, weak ferromagnetism which disappears below room temperature. According to the results by Anderson et al.¹⁶ on a synthetic single crystal (containing 3%

(16) P. W. Anderson, F. R. Merritt, J. P. Remeika, and W. A. Yager, Phys. Rev., 93, 717 (1954).

Fe^{2+}) the resonance absorption corresponding to this anisotropy goes down to zero rather abruptly in the range from 260 to 255°K., which is not easily explained on the basis of a change in the direction of the magnetic moments. Similar measurements by Kumazai et al.¹⁷ on a natural sample showed the transition

(17) H. Kumazai, H. Abe, K. Ono, I. Hagashi, J. Shinada, and K. Iwanaga, Phys. Rev., 99, 1116 (1955).

to take place at about 220°K., and less abruptly. Some spread in the transition temperature was also observed by neutron diffraction between synthetic and natural hematite,¹⁸ but there

(18) L. M. Corliss, J. M. Hastings, and J. E. Goldman, Phys. Rev., 93, 893 (1954).

was no noticeable effect of a magnetic field on the transition temperature or line intensity above and below the transition. Measurements of magnetostriction in hematite in the transition region have shown¹⁹ that the magnetostrictive effects are

(19) H. M. A. Urquhart and J. E. Goldman, Phys. Rev., 101, 1443 (1956).

closely related to the parasitic ferromagnetism, both having the same type of dependence on applied field strength and temperature.

On the basis of a saturation magnetization of 0.43emu/g.¹¹ the uncompensated magnetic moment is 0.006 Bohr magnetons per

iron atom, and possible explanations given by Néel⁴ about the origin of the parasitic ferromagnetism is that $\alpha\text{-Fe}_2\text{O}_3$ is a slightly defect structure, or that the sublattices inside a domain are not equivalent, either for geometrical reasons or on account of local fluctuations in composition. According to Li²⁰ the weak ferromagnetism observed in the (111) plane of

(20) Y.-Y. Li, Phys. Rev., 101, 1450 (1956).

hematite is identified with the magnetization in domain walls, pinned down by lattice imperfections. The disappearance of this ferromagnetism on cooling is interpreted as due to mutual annihilation and migration of the domain walls to the surface. On heating through the transition, the domain walls are re-created by nucleation and stabilized by the imperfection centers. It is considered extremely improbable that all the moments would turn 90° at the same temperature.

Ferric Oxide Sample.--The ferric oxide for this investigation was prepared by oxidizing "Iron by Hydrogen", Merck, in air at 1000°C. until constant weight was attained; this required eight hours. Iron determination gave 69.91% total iron (theoretical, 69.94%) and the ferrous content was found to be zero within the limits of error (0.05%). Spectrographic analysis showed the presence of about 0.01% Mn, less than 0.01% Al, Co, Mg, Ni, and Si, and less than 0.001% Ca, Cu, and Sn.

X-ray powder photographs of the product showed only lines from $\alpha\text{-Fe}_2\text{O}_3$. Its lattice constants ($\lambda\text{CoK}_{\alpha_1} = 1.78890 \text{ \AA.}$) were determined at about 25°C. in a 11.48 cm. diameter camera with asymmetric film mounting. The rhombohedral unit cell dimensions are $a = 5.4266 \text{ \AA.}$ and $\alpha = 55.256^\circ$, which agree very well with the values $a = 5.4271 \text{ \AA.}$ and $\alpha = 55.263^\circ$ (25°C.) found by Willis and Rooksby.²¹ The sample was found to be

(21) B. T. M. Willis and H. P. Rooksby, Proc. Phys. Soc. B, 65, 950 (1952).

slightly ferromagnetic with a moment of 0.36 gauss/g. at room temperature, i.e., of the same magnitude as reported by earlier investigators.¹¹⁻¹⁴

Experimental Technique.--The Mark I cryostat and the technique employed in low-temperature adiabatic calorimetry is described elsewhere.²² The copper calorimeter (laboratory

(22) E. F. Westrum, Jr. and A. F. Beale, Jr., to be published.

designation W-10) has a capacity of 92.8 cc.; it is gold-plated inside and out and has no vanes. The heat capacity of the empty calorimeter was determined separately, using the same thermometer and heater and exactly the same amount of indium-tin solder for sealing and Apiezon-T grease for thermal contact

with the thermometer and heater. It represented from 22 to 80% of the total heat capacity observed.

Temperatures were measured with a capsule-type platinum resistance thermometer (laboratory designation A-3) contained in an axial well in the calorimeter. The thermometer has been calibrated by the National Bureau of Standards, and the temperatures are judged to correspond with the thermodynamic temperature scale within 0.1°K. from 5 to 10°K. , within 0.03°K. from 10 to 90°K. , and within 0.04°K. from 90 to 350°K. Precision is considerably better, and the temperature increments are probably correct to 0.001°K. after corrections for quasi-adiabatic drift.

The calorimeter was loaded with 170.914 g. of the $\alpha\text{-Fe}_2\text{O}_3$ sample in a dry box filled with nitrogen. It was then evacuated and helium added at about 4 cm. Hg pressure at 25°C. to provide thermal contact between sample and calorimeter.

Results.--The heat-capacity determinations are listed in Table I in chronological order and expressed in terms of the thermochemical calorie, defined as 4.1840 absolute joules. The ice point was taken to be 273.15°K. and the atomic weight of iron as 55.85. The data are presented in terms of one mole of Fe_2O_3 , i.e., 159.70 g. An analytically-determined curvature correction was applied to the observed values of $\Delta H/\Delta T$. The approximate temperature increments can usually be inferred from the adjacent mean temperatures in Table I.

TABLE I
HEAT CAPACITY OF α -Fe₂O₃ IN CAL. DEG.⁻¹ MOLE⁻¹

T, °K.	C _p	T, °K.	C _p	T, °K.	C _p
Series I		Series II		Series IV	
58.61	2.612	223.58	20.17	5.58	0.0011
65.30	3.326	232.31	20.82	7.10	0.0024
73.20	4.248	241.06	21.44	7.87	0.0038
80.93	5.177	249.68	22.03	9.02	0.0073
88.57	6.128	258.22	22.57	10.31	0.0135
96.83	7.138	266.75	23.09	11.65	0.0218
106.36	8.308	275.38	23.61	13.02	0.0301
116.07	9.503	283.78	24.06	14.39	0.0390
121.39	10.15	292.35	24.50	15.72	0.0469
127.04	10.83	301.23	24.96	17.25	0.0583
133.82	11.63	310.20	25.42	18.97	0.0767
141.85	12.54	319.04	25.81	22.70	0.1406
150.70	13.52	327.77	26.19	24.65	0.1898
159.58	14.50	336.53	26.58	26.89	0.2567
168.38	15.38	345.42	26.94	29.24	0.3509
177.24	16.24			31.56	0.4473
185.88	17.05	Series III		34.80	0.6163
194.32	17.80			38.75	0.8662
202.65	18.52	6.97	0.0023	42.76	1.156
210.85	19.20			46.99	1.503
219.61	19.88			51.51	1.906
228.19	20.52			55.81	2.311
				59.71	2.729

The heat-capacity versus temperature curve is shown in Fig. 1. It has the usual sigmoid shape, with no sign of transitions, not even around 250°K. where the magnetic transition takes place. This indicates that the change in direction of easy magnetization does not involve any appreciable entropy increment, or that it is spread out over a rather broad temperature interval.

Values of C_p , S° , $H^\circ - H_0^\circ$, and $-(F^\circ - H_0^\circ)/T$ at selected temperatures are listed in Table II. The enthalpy, entropy, and free-energy increments were computed by numerical integration, using graphically interpolated values of heat capacity. The heat-capacity values are considered to have a probable error of about 5% at 5°K., 1% at 10°K., and 0.1% above 25°K. Values below 5°K. were extrapolated with a T^3 function. The effects of nuclear spin and isotopic mixing are not included in the entropy and free-energy functions and the values listed in Table II are therefore the conventional ones to be used in calculations of chemical equilibria. The estimated probable error in the thermodynamic functions is 0.1% above 100°K., but some of the values are given to an additional digit for comparison purposes.

The present measurements accord better with the data by Parks and Kelley³ on specular hematite and are 3% higher near 90°K. and within about 0.5% at higher temperatures. The present heat-capacity data are 2 to 6% higher

TABLE II
MOLAL THERMODYNAMIC FUNCTIONS OF $\alpha\text{-Fe}_2\text{O}_3$

T, °K.	C_p cal. deg. ⁻¹ mole ⁻¹	S° cal. deg. ⁻¹ mole ⁻¹	$H^\circ - H_0^\circ$ cal. mole ⁻¹	$-(F^\circ - H_0^\circ)$ cal. deg. ⁻¹ mole ⁻¹
5	0.0008	0.0003	0.001	0.00006
10	0.0120	0.0028	0.023	0.00046
15	0.0426	0.0134	0.158	0.0029
20	0.0912	0.0311	0.472	0.0075
25	0.1995	0.0618	1.171	0.0150
30	0.3812	0.1130	2.589	0.0267
35	0.6276	0.1890	5.072	0.0441
40	0.9532	0.2934	9.000	0.0684
45	1.334	0.427	14.69	0.101
50	1.768	0.590	22.43	0.141
60	2.742	0.996	44.82	0.249
70	3.868	1.502	77.77	0.391
80	5.066	2.097	122.44	0.567
90	6.307	2.765	179.28	0.773
100	7.528	3.492	248.44	1.008
110	8.765	4.268	329.88	1.269
120	9.984	5.083	423.64	1.553
130	11.18	5.930	529.5	1.857
140	12.34	6.801	647.2	2.178
150	13.45	7.690	776.1	2.516
160	14.54	8.594	916.1	2.868
170	15.56	9.506	1066.7	3.232
180	16.51	10.422	1227.1	3.605
190	17.42	11.340	1396.8	3.988
200	18.30	12.256	1575.4	4.379
210	19.13	13.169	1762.6	4.776
220	19.92	14.077	1957.8	5.178
230	20.66	14.979	2160.7	5.585
240	21.37	15.873	2370.9	5.994
250	22.04	16.760	2588.0	6.408
260	22.68	17.637	2811.7	6.823
270	23.29	18.504	3041.5	7.239
280	23.85	19.362	3277.2	7.658
290	24.39	20.208	3518.4	8.075
300	24.90	21.043	3764.9	8.493
350	27.12	25.054	5067	10.5
273.15	23.47	18.775	3115.1	7.370
298.15	24.80	20.889	3718.9	8.416

than those on the Kahlbaum sample. Inasmuch as even their specular hematite contained 0.5% H_2O and 0.5% SiO_2 and no attempt was made to correct for these impurities, the agreement must be considered satisfactory. Since the data on the specular crystals were used in calculating their published entropy, 21.5 ± 0.5 e.u., the entropy increment over the common region (90 to 295°K.) agrees quite well with that found in the present investigation and most of the difference of 0.6 e.u. is in the extrapolated portion as a consequence of the errors in their lowest temperature data.

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Figure Legend

Fig. 1. Molal heat capacity of $\alpha\text{-Fe}_2\text{O}_3$ from 5 to 350°K.