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The Crystal Structure of Manganese Diselenide and Manganese Ditelluride

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The properties of substances having the pyrite or similar type of structure have usually been interpreted as showing that in these compounds all the bonds are covalent. From x-ray data on pyrite, FeS_2 , hauerite, MnS_2 , skutterudite, CoAs_2 , etc., Pauling and Huggins¹ have obtained octahedral radii for metal atoms in the transition groups of the third and fourth rows of the periodic table. They observed that the radius of manganese in hauerite and manganese ditelluride, 1.55–1.59 Å., did not agree with the radius, 1.15 Å., obtained by extrapolating the sequence $\text{Ni}^{\text{II}} \text{Co}^{\text{II}} \text{Fe}^{\text{II}} \text{Mn}^{\text{II}}$. A safer extrapolation of the isoelectronic sequence $\text{Ni}^{\text{IV}} \text{Co}^{\text{III}} \text{Fe}^{\text{II}} \text{Mn}^{\text{I}}$ gave a value 1.24 Å. for Mn^{I} which should be an upper limit for Mn^{II}

and studied by means of x-rays. The results are described in this paper. The discussion of the experimental data includes an interpretation of the magnetic susceptibility measurements made on these and related compounds by Haraldsen and Klemm.⁴

The compounds were prepared by sealing stoichiometric proportions of the elements in evacuated Pyrex glass tubes and heating these in a furnace at 550° for forty-eight hours.

Powder photographs were taken of manganese diselenide and manganese ditelluride using copper radiation filtered through nickel. The photographs are reproduced in Figs. 1 and 2. As both manganese disulfide and manganese ditelluride

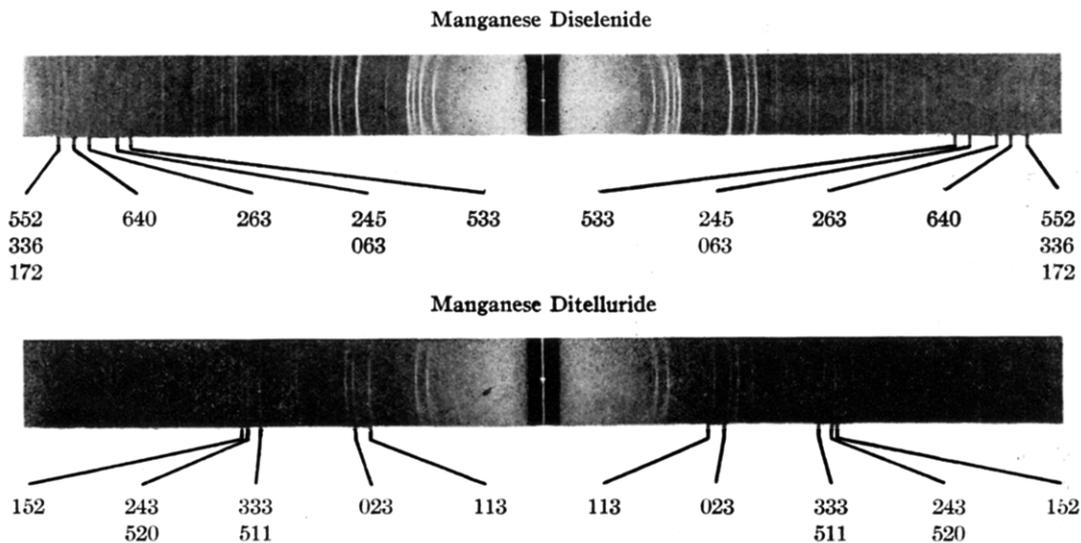


Fig. 1.

The parameter in hauerite was redetermined by Offner² as a check on the discrepancy. The value found gave a sulfur radius in excellent agreement with the one assumed by Pauling and Huggins¹ but did not remove the anomaly of the large manganese radius.

In order to extend the investigation to other compounds, the substances manganese diselenide and manganese ditelluride³ have been prepared

(1) Linus Pauling and M. L. Huggins, *Z. Krist.*, **87**, 205 (1934).

(2) Franklin Offner, *ibid.*, **89**, 182 (1934).

(3) The structure of manganese ditelluride has been determined by Oftedal, *Z. physik. Chem.*, **135**, 291 (1928). In the present investigation a more accurate parameter determination has been made.

are known to have the pyrite structure, it was assumed that manganese diselenide also has this structure. The photographs were indexed on the basis of cubic units. Weak extraneous lines were accounted for by the presence of small amounts of manganese selenide and selenium or manganese telluride and tellurium.^{4a} Data which were used in determining the selenium and tellurium positions are given in Tables I and II.

(4) Haraldsen and Klemm, *Z. anorg. Chem.*, **223**, 409 (1935).

(4a) Since the writing of this paper pure manganese diselenide has been prepared. X-ray powder photographs of this preparation do not show the extraneous lines observed in earlier work.

TABLE I
MANGANESE DISELENIDE

Copper radiation. $\lambda_\alpha = 1.539 \text{ \AA}$. Camera radius 5.005 cm.

2D, cm.	θ	Sin θ	hkl	I , obsd.	I , calcd.
4.19	0.2095	0.2080	111	10	8
4.84	.2420	.2397	200	144	144
5.42	.2710	.2677	210	214	226
5.95	.2975	.2932	211	214	214
6.92	.3460	.3391	220	55	52
8.57	.4285	.4155	222	16	14
8.94	.4470	.4322	320	120	120
9.30	.4650	.4484	321	145	145
10.01	.5005	.4797	400	18	19
10.33	.5165	.4989	322 410	16	15
11.00	.5500	.5227	331	6	6
11.32	.5660	.5363	420	2	3
11.63	.5815	.5492	421	50	44
12.55	.6275	.5871	422	8	8
13.15	.6575	.6112	510	9	11
13.44	.6720	.6225	333 511	76	80
14.02	.7010	.6450	432 520	52	55
14.32	.7160	.6565	521	28	30
14.90	.7450	.6780	440	40	44
16.05	.8025	.7190	442 600	18	15
16.35	.8175	.7294	610	7	7
17.48	.8740	.7669	443 540 621	14	15
18.09	.9045	.7860	533	10	10
18.68	.9340	.8040	542 630	14	14
19.91	.9955	.8391	632	16	16
20.55	1.0275	.8560	551 711	16	15
20.88	1.0440	.8645	640	38	38
21.55	1.0775	.8807	633 721 552	40	40
23.41	1.1705	.9209	731 553	42	43

TABLE II
MANGANESE DITELLURIDE

Copper radiation. $\lambda_\alpha = 1.539 \text{ \AA}$. Camera radius 5.005 cm.

2D, cm.	θ	Sin θ	hkl	I , obsd.	I , calcd.
5.01	0.2505	0.2480	210	198	207
5.50	.2750	.2722	112	208	183
7.54	.3770	.3681	113	99	99
8.24	.4120	.4003	023	87	87
8.57	.4285	.4140	132	117	117
9.20	.4600	.4440	400	18	24
10.67	.5335	.5085	241	45	48
10.95	.5475	.5206	332	24	24
11.48	.5740	.5430	422	3	4
12.29	.6145	.5766	333 511	45	43
12.81	.6405	.5975	432 520	45	48
13.07	.6535	.6080	521	27	30
13.57	.6785	.6275	440	33	36
15.07	.7535	.6841	532 611	33	36

The unit cells of pyrite type structures contain four molecules and have atomic positions defined by the following coordinates of T_h^8 :

- R: 0 0 0; $\frac{1}{2} \frac{1}{2} 0$; $\frac{1}{2} 0 \frac{1}{2}$; $0 \frac{1}{2} \frac{1}{2}$
 X: $u \ u \ u$; $\frac{1}{2} + u, \frac{1}{2} - u, \bar{u}$; $\bar{u}, \frac{1}{2} + u, u - u$; $\frac{1}{2} - u, \bar{u}, \frac{1}{2} + u$
 $\bar{u} \ \bar{u} \ \bar{u}$; $\frac{1}{2} - u, \frac{1}{2} + u, u$; $u, \frac{1}{2} - u, \frac{1}{2} + u$; $\frac{1}{2} + u, u, \frac{1}{2} - u$

The structure factor for the reflection (hkl) with h, k , and l all odd or all even is $F = 4f_R + 8f_X \cos 2\pi hu \cos 2\pi ku \cos 2\pi lu$ and for h, k even and l odd or h, k odd, l even $F = 8f_X \cos 2\pi hu \sin 2\pi ku \sin 2\pi lu$.

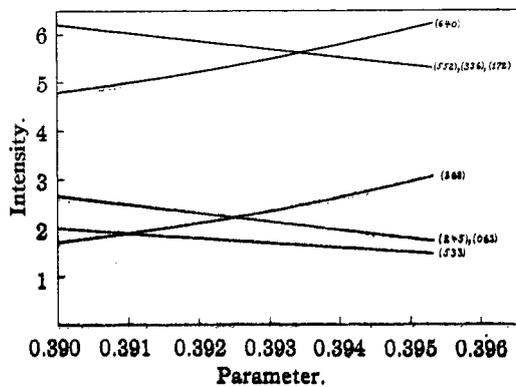


Fig. 2.

The calculated intensities in the sixth columns of Tables I and II are given by the equation

$$I \sim \frac{1 + \cos^2 \theta}{\cos \theta \sin^2 \theta} hF^2$$

where h is the frequency factor. The atomic scattering factors used are those of Pauling and Sherman.⁵

The relative observed intensities in the fifth columns were obtained from microphotometer records of the photographs. The estimated accuracy of these results is about $\pm 20\%$.

For convenience in making comparisons the lattice constants, parameters, and interatomic distances found for hauerite, manganese diselenide, and manganese ditelluride are shown in Table III. The value of the manganese diselenide parameter is limited to a narrow region, 0.3912–0.3935, by the comparisons (263) > (533), (127) + (336) + (552) > (640), and (263) = (245) + (063). Similarly the comparisons (113) > (023), (520) + (243) = (511) + (333), and (152) = $\frac{3}{5}$ {(520) + (243)} require the manganese ditelluride parameter to lie between 0.384 and 0.388. The intensities of these reflections as functions of the parameters are shown in Figs. 2 and 3 for the diselenide and ditelluride, respectively.

The agreement found between observed and calculated intensities of manganese diselenide and ditelluride for the parameter values given in Table III may be seen in Figs. 4 and 5. The lengths of the vertical lines represent relative

(5) Linus Pauling and J. Sherman, *Z. Krist.*, **51**, 1 (1932).

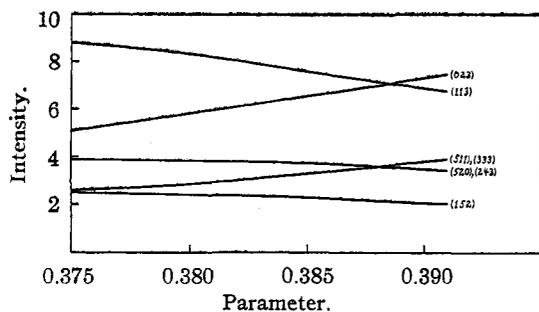


Fig. 3.

observed intensities, the cross bars show the calculated intensities.

TABLE III

Compound	Unit cell dimension, Å.	Parameter	Mn-X distance, Å.	X-X distance, Å.
MnS ₂	6.097 ± 0.005 ¹	0.4012 ± 0.0004 ²	2.59	2.086 ± 0.008
MnSe ₂	6.417 ± 0.005	.393 ± 0.001	2.70	2.38 ± 0.02
MnTe ₂	6.943 ± 0.002 ³	.386 ± 0.002	2.90	2.74 ± 0.05

The sulfur-sulfur, selenium-selenium, and tellurium-tellurium distances found in hauerite, manganese diselenide, and manganese ditelluride are 2.086 ± 0.008, 2.38 ± 0.02, and 2.74 ± 0.05 Å., respectively. The corresponding covalent radii of sulfur, selenium, and tellurium are half these distances. In Table IV the observed radii are

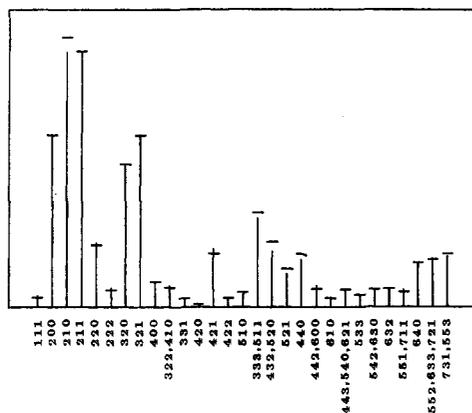


Fig. 4.

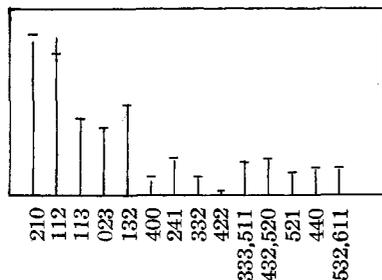


Fig. 5.

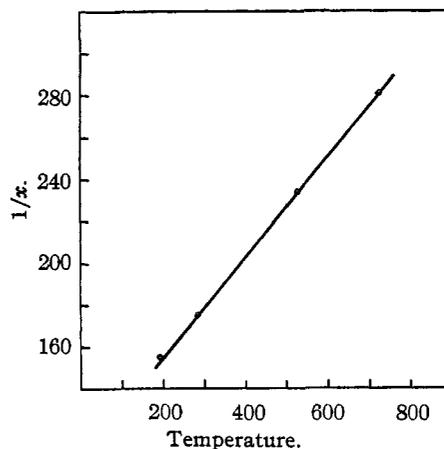
compared with the tetrahedral and the normal valence covalent radii of Pauling and Huggins.¹

If the compounds under investigation were covalent, the observed radii would be expected to agree well with the tetrahedral radii of Table IV. However, the agreement is distinctly better with the normal valence radii, suggesting that each non-metal atom is forming only one covalent bond and that the manganese-non-metal bond is, therefore, an ionic bond.

TABLE IV

Element	Tetrahedral radius, Å.	Normal valence radius, Å.	Observed radius, Å.
Sulfur	1.04	1.04	1.043 ± 0.004
Selenium	1.14	1.17	1.19 ± 0.01
Tellurium	1.32	1.37	1.37 ± 0.02

It should be possible by means of magnetic susceptibility measurements, as discussed by Pauling,⁶ to distinguish between covalent d^2sp^3 bonds and ionic bonds. Divalent manganese ion has five odd electrons filling the five 3d orbitals, with a resultant spin moment $\mu = 5.92$ Bohr magnetons. If the bonds are covalent, however, two of the 3d orbitals are used in bond formation; two of the odd electrons must therefore pair, leaving only three unpaired with a spin moment $\mu = 3.88$ Bohr magnetons.

Fig. 6.—MnS: $\Delta = 460$; $\mu = 5.87$.

Magnetic susceptibility measurements have been made by Haraldsen and Klemm^{7,8} on several sulfides, selenides, and tellurides of manganese, cobalt, and nickel over a wide range of temperatures. As shown by Figs. 6, 7, 8, and 9, the magnetic susceptibilities follow the Weiss-Curie law

$$X = c/(T + \Delta)$$

(6) Linus Pauling, *THIS JOURNAL*, **53**, 1391 (1931).(7) Haakon Haraldsen and Wilhelm Klemm, *Z. anorg. Chem.*, **220**, 183 (1934).(8) Haakon Haraldsen and Wilhelm Klemm, *ibid.*, **223**, 409 (1935).

The values of Δ may be obtained from the graphs. The magnetic moments are then calculated from the equation

$$\mu = 2.84 \sqrt{X_{\text{mol.}} (T + \Delta)}$$

The moments found for manganous sulfide and manganese disulfide are 5.87 and 6.13. The values are very close to the value 5.92 predicted for divalent manganese ion and are in definite disagreement with the presence of d^2sp^3 bonds in either compound. Since alabandite, manganous sulfide, has been shown by Wyckoff⁹ to have the rock-salt structure or one very similar, a moment of about 5.92 was to be expected. The experimental value, 5.87, not only substantiates Wyckoff's⁹ structure determination, but, in addition, it confirms the present interpretation of Haraldsen and Klemm's^{7,8} magnetic susceptibility measurements.

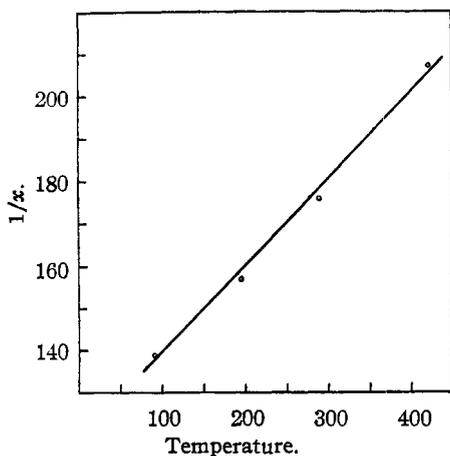


Fig. 7.— MnS_2 : $\Delta = 528$; $\mu = 6.13$.

The observed moment of cobalt disulfide, 1.99, is in agreement with the assumption that here the cobalt is forming octahedral d^2sp^3 bonds, the predicted spin moment in this case being 1.73. The moment observed for nickel disulfide does not permit a decision to be made regarding the type of bond between the nickel and sulfur. Either ionic or covalent octahedral bonds leave the nickel atom with two odd electrons and a predicted moment of 2.83 Bohr magnetons which is close to the observed value, 2.71. The comparison of the covalent radii of the transition elements made earlier in this paper leads, however, to the natural supposition that in nickel disulfide the nickel-sulfur bonds are covalent also.

The anomalous manganese radius may thus

(9) Wyckoff, *Am. J. Sci.*, **2**, 239 (1921).

be accounted for readily by saying the bonds of manganese in pyrite type structures are essentially ionic while those of iron, cobalt, and nickel are essentially covalent.

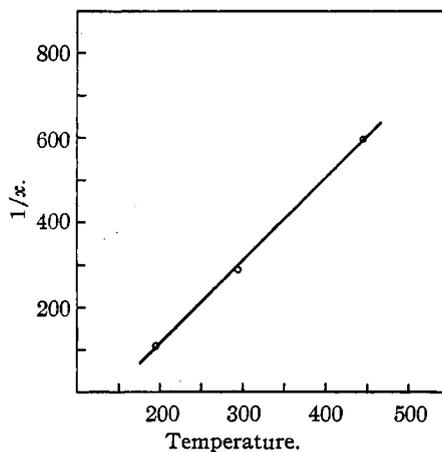


Fig. 8.— CoS_2 : $\Delta = -150$; $\mu = 1.99$.

Another explanation suggested by Professor Pauling is that the manganese bonds resonate between ionic and sp^3d^2 bonds, the sp^3d^2 bonds involving $4d$ rather than $3d$ orbitals. In this case a non-metal-non-metal distance intermediate between the sum of the tetrahedral and the sum of the normal valence covalent radii would be expected. It may be concluded from the observed selenium-selenium and tellurium-tellurium distances in manganese diselenide and ditelluride that the amount of resonance is rather small.

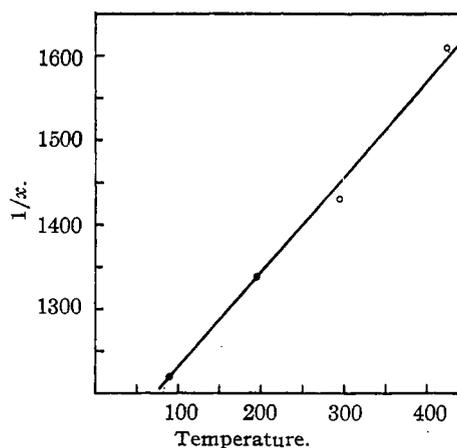


Fig. 9.— NiS_2 : $\Delta = 1025$; $\mu = 2.71$.

It is interesting to note that further tests may be made on cobalt and nickel diselenide and ditelluride. If these compounds are covalent the selenium-selenium and tellurium-tellurium distances should agree closely with the sum of the

tetrahedral radii for these elements. These values, 2.28 and 2.64 Å., would be shorter than the distances observed in the corresponding manganese compounds. It is planned to prepare several of these substances and to investigate their magnetic susceptibilities and crystal structures in these Laboratories.

Acknowledgment.—The author wishes to thank Professor Linus Pauling for his interest and help in this investigation; his suggested interpretation of the magnetic measurements of Haraldsen and Klemm proved especially valuable. The author also wishes to thank Dr. James H. Sturdivant for his kind advice concerning the preparation of the powder photographs.

Summary

The crystal structures of manganese diselenide and manganese ditelluride have been investigated

with x-rays and found to belong to the pyrite type of structure. The cubic unit of manganese diselenide has the dimension $a_0 = 6.417 \pm 0.005$ Å. and the parameter $u = 0.393 \pm 0.001$. For manganese ditelluride the corresponding values are $a_0 = 6.943 \pm 0.002$ Å. and $u = 0.386 \pm 0.002$.

The results obtained suggest that in the pyrite type structures the manganese–non-metal bonds are either ionic or resonate between ionic and covalent, the covalent part involving $4d$ orbitals from the manganese rather than $3d$ orbitals.

The magnetic susceptibility measurements of Haraldsen and Klemm,^{7,8} on the sulfides of manganese, cobalt, and nickel, are interpreted as supporting the results of the X-ray investigation, and, further, as showing that cobalt and nickel probably form covalent d^2sp^3 bonds in these compounds.

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Comparison of Platinum–Rhodium Resistance Thermometers with the Helium Gas Thermometer from 11 to 300°K. An Improved Cryostat. Low Temperature Studies, No. 2

BY R. W. BLUE AND J. F. G. HICKS, JR.

Introduction

In the program of low temperature research now in progress in this Laboratory a prominent place has been assigned to the precise measurement of specific heats. The establishment of an accurate and reliable secondary temperature scale is of fundamental importance in these measurements. The purpose of this paper is to describe the construction and calibration of resistance thermometers and thermocouples for use as secondary standards.

The cryostat used for this research embodies several important features of the apparatus described by Southard and Brickwedde,¹ while the arrangement of radiation shields and reservoirs follows closely that employed by Keyes, Gerry and Hicks² in the hydrogen liquefier described recently. The method which we used for transferring refrigeration was suggested by an apparatus of Mendelssohn, Ruhemann and Simon.³

(1) Southard and Brickwedde, *THIS JOURNAL*, **55**, 4378 (1933).

(2) Keyes, Gerry and Hicks, *ibid.*, **59**, 1426 (1937).

(3) Mendelssohn, Ruhemann and Simon, *Z. Physik. Chem.*, **153**, 121 (1931).

Since the cryostat has some advantages over those in common use and is readily adaptable for many kinds of low temperature measurements, it is described here in considerable detail.

Construction of Resistance Thermometers.—As secondary standards for specific heat work we have chosen platinum–10% rhodium resistance thermometers of the strain-free type, described by Meyers.⁴ That such thermometers are suitable for low temperature specific heat measurements has been demonstrated by Southard, Brickwedde and Milner.⁵ Platinum–10% rhodium wire has a relatively high resistivity and a satisfactory temperature coefficient of resistance. The residual resistance at low temperatures is sufficiently high to permit the thermometers to be used readily as heaters. Four resistance thermometers were calibrated. They were designated by their nominal ice-point resistances, R197, R222, R140 and R145. Number 40 B. and S. gage wire was used for all thermometers. R197 and R222 were wound on mica crosses ($7.5 \times 0.8 \times 0.01$ cm.) each of which was enclosed in a copper tube (9 cm. long \times 1.3 cm. o. d.; wall thickness 0.2 cm.). The ends were closed with copper disks, the top disk being fitted with four platinum tubes through which the leads were sealed with lead glass. The upper disk

(4) Meyers, *Bur. Standards J. Research*, **9**, 807 (1932).

(5) Southard and Milner, *THIS JOURNAL*, **55**, 4984 (1933).