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Magnetic Structures of the Polymorphic Forms of Manganous Sulfide*

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Manganous sulfide exists in three polymorphic forms. There are two cubic modifications, α-MnS having the rock salt structure and β-MnS with the zinc blende structure. The third form is hexagonal β-MnS with the wurtzite structure. The magnetic susceptibilities of all three forms and the antiferromagnetic structures, as determined by neutron diffraction, are reported. α-MnS exhibits ordering of the second kind, in agreement with earlier work. The spin direction, however, is found to be in the ferromagnetic (111) sheets rather than along cube edges. In the cubic β-MnS case, the magnetic structure is the hitherto unobserved "improved ordering of the first kind" proposed by Anderson. The spin direction is normal to the unique cubic axis. The hexagonal β-MnS antiferromagnetic structure can be derived from the cubic β-MnS by stacking the close-packed (111) sheets of the zinc blende form according to the scheme *ABA*—appropriate to hexagonal close-packing. The magnetic unit cell is *ortho*hexagonal with $a_0'=a_0\sqrt{3}$, $b_0'=2a_0$, $c_0'=c_0$, where the unprimed symbols refer to the original hexagonal cell. The spin direction is normal to the (011) plane. These magnetic structures are discussed on the basis of an indirect exchange coupling mechanism.

THE neutron diffraction experiments of Shull, Strauser, and Wollan[1] on MnO have indicated that an indirect exchange mechanism is required to explain the observed antiferromagnetic structure. In this case, the observed magnetic scattering was interpreted as showing that next-nearest neighbor Mn^{++} ions, which in the NaCl structure are separated by an intervening $O^{=}$ ion, are coupled antiferromagnetically. Theoretical studies[2] have made plausible the idea that indirect exchange proceeds via excited states of the intermediate anion. Anderson,[2] in particular, has emphasized that this indirect exchange must be expected to show the directional properties of the orbitals in the outer shell of the nonmagnetic connecting ions. Manganous sulfide, because it exists in three simple polymorphic forms, provides a convenient system for studying the role of the nonmagnetic ion in determining the magnetic coupling scheme.

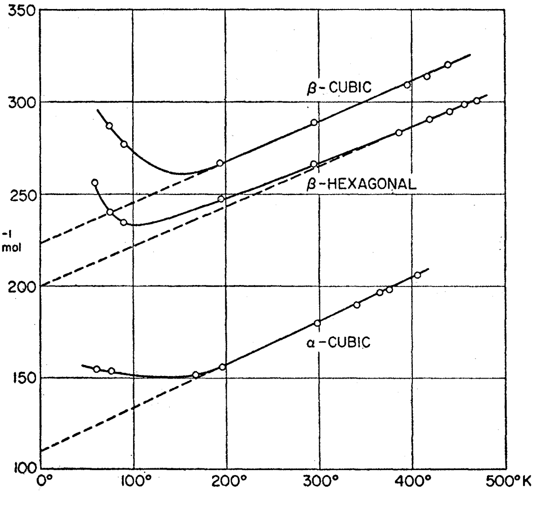

FIG. 1. Magnetic susceptibility of MnS.

The three crystalline modifications of MnS are the NaCl structure (α-MnS), the zinc blende structure (β-MnS), and the wurtzite structure (β-MnS). The first two are face-centered cubic and the last hexagonal. All three may be considered as derived from one of the forms of closest packing of Mn^{++} ions, with the $S^{=}$ ions placed either in octahedral sites (NaCl structure) or tetrahedral sites (zinc blende and wurtzite structures). The two β forms can be conveniently, although somewhat artifically, considered as composed of Mn_4S tetrahedra stacked according to the demands of cubic or hexagonal close-packing.

Thus each Mn^{++} ion has twelve nearest Mn^{++} neighbors in all three forms but different numbers of $S^{=}$ neighbors, six $S^{=}$ ions in the NaCl structure and $4S^{=}$ ions in the zinc blende and wurtzite structures. The arrangement of sulfur in α-MnS is such that each manganese is bonded via a sulfur atom to its twelve nearest neighbors by 90° Mn—S—Mn ligands and to its six second nearest manganese neighbors by 180° Mn—S—Mn ligands, all of equal length. In the β forms each manganese is bonded tetrahedrally through sulfur atoms to its twelve nearest manganese neighbors only.

Published magnetic susceptibility data for all three allotropic forms show them to be antiferromagnetic with Néel temperatures in the range 75°–150°K. At elevated temperatures the susceptibilities are given by a Curie-Weiss law, and the magnetic moments correspond to five unpaired electron spins on the Mn^{++} ions. Shull, Strauser, and Wollan[1] have examined the structure of the α-MnS below the Néel temperature by neutron diffraction, and have reported the antiferromagnetic structure to be the same as that found for MnO.

All three polymorphic forms of MnS have been prepared by us for the purpose of neutron diffraction

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[1] C. G. Shull and J. S. Smart, Phys. Rev. **76**, 1256 (1949); Shull, Strauser, and Wollan, Phys. Rev. **83**, 333 (1951).

[2] H. A. Kramers, Physica **1**, 182 (1934); P. W. Anderson, Phys. Rev. **79**, 350 (1950); G. W. Pratt, Jr., Phys. Rev. **97**, 926 (1955).

Table I. Magnetic susceptibility of MnS as a function of temperature.

Form											
α-cubic	T(°K)	61	76	167	195	298	340	365	375	405	
	$\chi_{\text{mol}}\times10^6$	6450	6500	6600	6420	5560	5270	5085	5050	4855	
β-cubic[a]	T(°K)	76	91	195	295	396	417	440			
	$\chi_{\text{mol}}\times10^6$	3490	3610	3750	3470	3240	3190	3130			
β-hexagonal	T(°K)	59	76	91	195	295	386	419	441	457	471
	$\chi_{\text{mol}}\times10^6$	3900	4165	4265	4040	3765	3540	3450	3400	3355	3330

[a] Corrected for the presence of hexagonal phase.

and magnetic susceptibility studies. The α-MnS is the stable form, and is easily prepared in a pure state. With some alteration of Schnaase's[3] method, the hexagonal β modification was prepared in pure form also. Cubic β-MnS, however, contained approximately 13.5% of the hexagonal structure from examination of the x-ray and neutron diffraction patterns.

The unit cell dimensions of both β modifications were determined using Cr Kα radiation. For cubic β-MnS, $a_0=5.606\pm0.003$ A. For hexagonal β-MnS, $a_0=3.987\pm0.003$ A and $c_0=6.438\pm0.003$ A. These measurements are in quite good agreement with those of Mehmed and Haraldsen.[4]

Magnetic susceptibility measurements were made, using a Gouy balance, on α- and β-MnS in the temperature range 60°–470°K. This seemed particularly desirable in the case of the β forms because previous authors have not reported the purity of their specimens with regard to admixture of cubic and hexagonal structures. The results are given in Table I and Fig. 1.

Above room temperature the various modifications of manganous sulfide obey the Curie-Weiss law,

$$\chi=C/(T+\theta).$$

Values of the constants calculated from our data are given in Table II.

Neutron Diffraction Measurements

Neutron diffraction patterns for the three polymorphic forms of MnS taken at 4.2°K and a wavelength of 1.064 A are shown in Figs. 2, 3, and 4. In all three patterns, magnetic superstructure peaks are clearly in evidence, indicating the occurrence of three distinct antiferromagnetic structures. The diffraction peaks labeled "nuclear" are the fundamental peaks and persist unchanged above the Néel point, except for a small Debye-Waller temperature correction. The superstructure peaks are entirely magnetic in origin and disappear when the temperature exceeds the Néel point.

Table II. Curie-Weiss constants for MnS.

Form	C	θ (°K)
α-cubic	4.23	465
β-cubic	4.46	982
β-hexagonal	4.66	932

The magnetic diffraction pattern for the rock salt form of MnS is exactly the same as one finds for MnO. The nuclear intensities are of course different in the two cases inasmuch as the scattering amplitudes of sulfur and oxygen are not the same. As in the case of MnO, the magnetic lines can be indexed on a cubic unit cell whose edge is twice that of the chemical cell. The antiferromagnetic structure corresponds to ordering of the second kind and is pictured in Fig. 5. In this structure, the moments within a given (111) plane are ferromagnetically aligned and successive (111) planes form an antiferromagnetic sequence in which adjacent planes have oppositely directed moments. The orientation of the moments relative to the crystal axes cannot be completely specified in this case from powder data. However, the detailed agreement of calculated and observed intensities as indicated in Table III requires the moments to lie in the (111) sheets.[5]

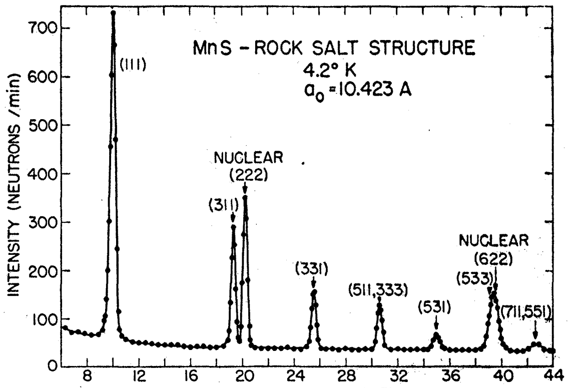

Fig. 2. Neutron diffraction pattern of α-MnS (rock salt form).

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[3] H. Schnaase, Z. physik. Chem. **B20**, 89 (1933).

[4] F. Mehmed and H. Haraldsen, Z. anorg. u. allgem. Chem. **235**, 193 (1938).

[5] This result disagrees with the earlier work of Shull, Strauser, and Wollan[1] in which the moment direction was taken to be parallel to a cube edge. For purposes of comparison, intensity calculations based on this model have been included in Table III. Recent studies, both by the authors (unpublished) and by W. L. Roth [Abstracts of the American Crystallographic Association annual meeting, 1956 (unpublished)], indicate that in MnO as

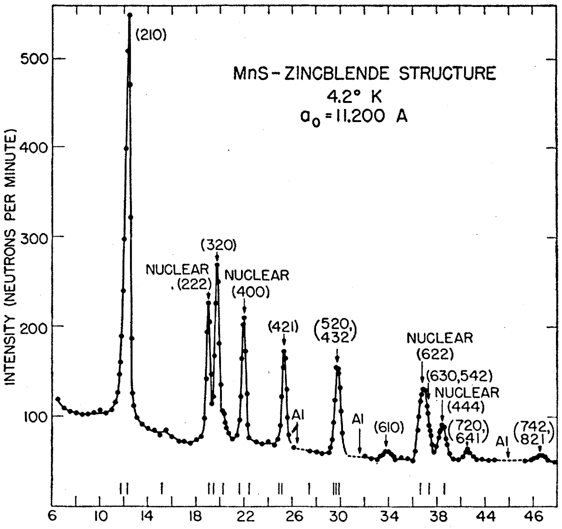

FIG. 3. Neutron diffraction pattern of β-MnS (zinc blende form). The sample used contained 13.5% of the hexagonal modification of β-MnS. The contributions of this contamination to the diffraction pattern are indicated by the vertical bars at the bottom of the figure. The symbol Al refers to lines produced by the aluminum sample holder.

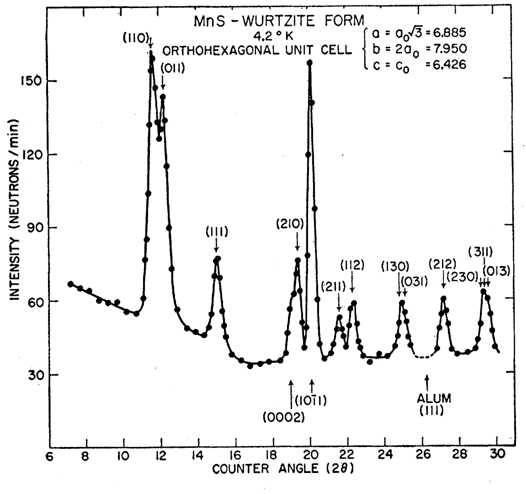

FIG. 4. Neutron diffraction pattern of β-MnS (wurtzite form). The nuclear peaks are indexed on the original hexagonal cell and are shown below the diffraction pattern.

TABLE III. Calculated and observed integrated intensities for magnetic peaks of α-MnS (rock salt form).

hkl	Observed intensities	Calculated intensities Moments in (111) plane	Calculated intensities Moments ‖ to cube edge
111	2798	2741	1827
311	808	784	1015
331	434	434	402
511, 333	326	329	257
531	178	182	224
533	obscured	39	52
711, 551	65	65	59

The diffraction pattern of the zinc blende form of MnS is strikingly different from that of α-MnS despite the fact that the spatial arrangement of the manganese atoms is unchanged. While in the case of the rock salt form the superstructure lines appear only for h, k, l odd, the rule for the zinc blende form is that two indexes be even and one odd, and that $h \neq k \neq l$. This indexing scheme, based on a cubic unit cell with twice the linear dimensions of the "chemical" cell, identifies the structure as ordering of the third kind, a type recently suggested by Anderson,[6] but hitherto unobserved. It is shown schematically in Fig. 5. The magnetic moments lie in a plane perpendicular to the unique crystallographic direction (the x direction of the figure). A comparison of observed and calculated intensities for this model is presented in Table IV.

In the case of the hexagonal or wurtzite form of β-MnS the superstructure lines can be indexed on an orthohexagonal cell for which $a_0' = a_0\sqrt{3}$, $b_0' = 2a_0$, $c_0' = c_0$, where the unprimed symbols refer to the original hexagonal cell. The magnetic moment arrangement deduced from the diffraction data is shown in Fig. 6. Table V compares the observed intensities with those computed for this model. The moment direction was taken to be normal to the (011) plane.

The magnetic structures described above were first established by calculating intensities with the aid of an approximate form factor curve obtained from studies of other iron-group compounds. Correct form factor values were then obtained for each reflection by comparing the observed and calculated structure factors. A plot of these points for all three polymorphic forms is shown in Fig. 7. The final intensities were then calculated using the smooth curve drawn through the points. Included in Fig. 7 are points taken from a

TABLE IV. Calculated and observed integrated intensities for magnetic peaks of β-MnS (zinc blende form).

hkl	Calculated intensities	Observed intensities[a]
210	840	818
320	328	334
421	180	175
520, 432	195	190
610	24	29
630, 542	71	81
720, 641	34	28
742, 821	18	16

[a] Corrected for hexagonal contamination.

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well, the moments lie in or very close to the (111) sheets. A consequence of these findings both for α-MnS and MnO is that alternative structures such as those proposed by Y.-Y. Li [Phys. Rev. **100**, 627 (1955)] are no longer capable of explaining the observed data. Li's structures as well as a random substructure model require that $\langle q^2 \rangle_{hkl}$, the direction factor for magnetic scattering averaged over the nonzero reflections of the crystallographic form, have the value 2/3 for all h, k, and l. For spins lying in the (111) plane, the $\langle q^2 \rangle$ values for the first two reflections are in fact $\langle q^2 \rangle_{111} = 1$ and $\langle q^2 \rangle_{311} = 17/33$.

[6] P. W. Anderson, Phys. Rev. **79**, 705 (1950).

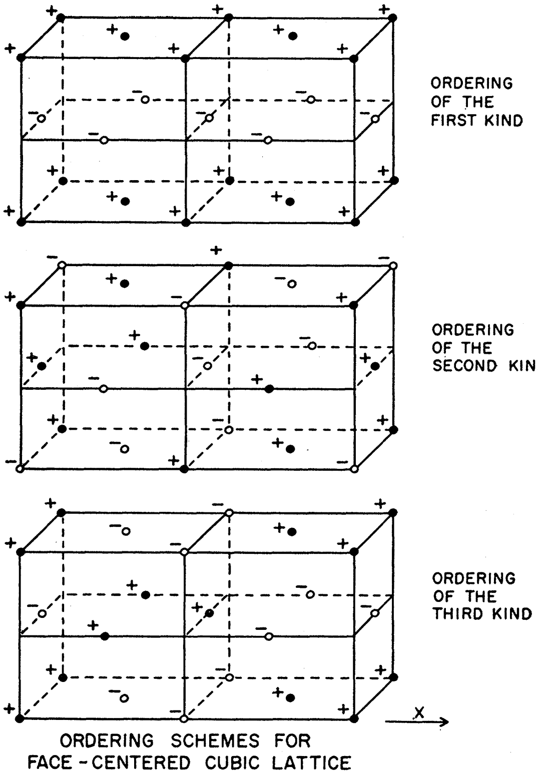

FIG. 5. Possible ordering schemes for the face-centered cubic lattice. Only the sites occupied by magnetic atoms have been indicated.

reinvestigation by the authors of MnO. It is interesting to note that they are well represented, as one might expect, by the MnS form factor curve.

DISCUSSION

The theory of antiferromagnetism in the face-centered cubic lattice has been treated by several authors.[6–8] Three possible ordering schemes, shown in Fig. 5, have been discussed. A significant basis for classification of these ordering schemes is one involving the nearest and next-nearest neighbor configurations. In ordering of the first kind, which is a spin layer structure, two-thirds of the nearest neighbors of any ion are coupled antiferromagnetically; the remainder of the nearest neighbors as well as all the next-nearest neighbors are coupled ferromagnetically. Ordering of the second kind is characterized by having half the nearest neighbors antiferromagnetically and half ferromagnetically coupled to the central ion, resulting in zero mean correlation between nearest neighbors. All next-nearest neighbors, in ordering of the second kind, are coupled antiferromagnetically. The last scheme, ordering of the third kind, has the same nearest neighbor configuration as ordering of the first kind, namely two-thirds antiparallel, one-third parallel. The next-nearest neighbors, however, are arranged one-third antiparallel, two-thirds parallel, instead of all parallel as in

TABLE V. Calculated and observed integrated intensities for magnetic peaks of β-MnS (wurtzite form).

hkl	Calculated intensities	Observed intensities
110 011	860	861
111	142	147
210	154	146
211	65	67
112	103	88
130 031	99	106
131	32	obscured
212	67	82
230 311 013	134	130

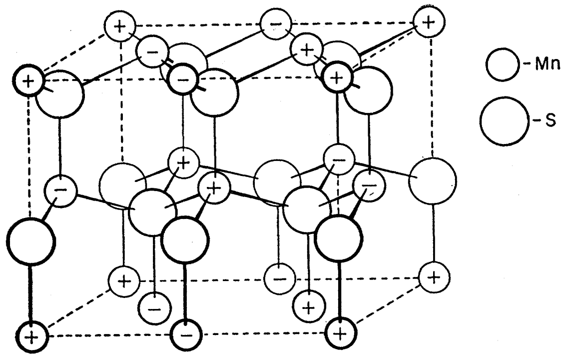

FIG. 6. Magnetic structure of β-MnS (wurtzite form). The orthohexagonal unit cell is shown.

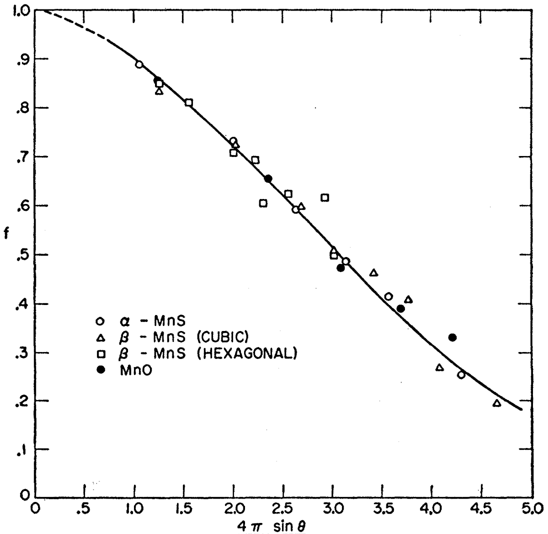

FIG. 7. Magnetic form factor for Mn^{++}. The curve represents the smoothed value used in obtaining the calculated magnetic intensities shown in Tables III, IV, V.

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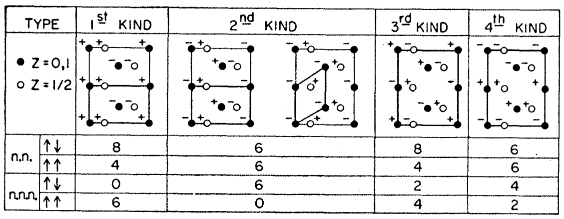
[7] J. S. Smart, Phys. Rev. **86**, 968 (1952).

[8] J. H. Van Vleck, J. phys. radium **12**, 262 (1951).



TYPE		1st KIND	2nd KIND	3rd KIND	4th KIND
n.n.	↑↓	8	6	8	6
	↑↑	4	6	4	6
n.n.n.	↑↓	0	6	2	4
	↑↑	6	0	4	2

FIG. 8. Possible ordering schemes for the *ortho*hexagonal lattice. Only the sites occupied by magnetic atoms have been indicated. The smallest magnetic unit cell is shown in heavy lines. The number of parallel and antiparallel nearest (n.n.) and next-nearest (n.n.n.) neighbors are tabulated for each type of ordering.

ordering of the first kind. Because of this enhanced antiparallel correlation, ordering of the third kind has been called "improved ordering of the first kind."[8]

The rock salt form of MnS, as has been mentioned, has an antiferromagnetic spin arrangement corresponding to ordering of the second kind. Hence the spin coupling is between next-nearest neighbors. This can be accounted for by invoking an indirect exchange mechanism which should be rather favorable for this structure since the next-nearest neighbors and the intermediate anion lie along a straight line. The cubic β-MnS has exactly the same magnetic ion structure (cubic close packing) as α-MnS, but the anions have been shifted to the tetrahedral sites. In this structure the intermediate anion now connects nearest neighbors through the tetrahedral angle. Hence, if the indirect exchange mechanism is operative, one would expect a coupling scheme involving a nearest neighbor correlation. Indeed, the zinc blende form or cubic β-MnS was found to have ordering of the third kind in which two-thirds of the nearest neighbors are antiparallel and one-third parallel while next-nearest neighbors are arranged one-third antiparallel, two-thirds parallel.

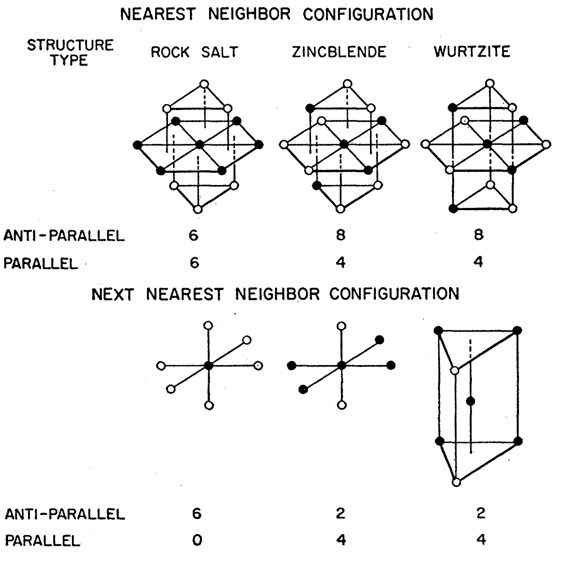


FIG. 9. Metal-metal nearest neighbor and next-nearest neighbor configurations for the three polymorphic forms of MnS.

The other form of β-MnS is a hexagonal close-packed arrangement of the magnetic ions with the anions occupying tetrahedral sites as in the cubic β-MnS. As has been mentioned, the magnetic diffraction pattern which one observes can be indexed using an *ortho*hexagonal unit cell which has four times the volume of the original "chemical" unit cell. A classification scheme based on the nearest and next-nearest neighbor spin configurations can be developed for an *ortho*hexagonal lattice. Figure 8 shows all the possible arrangements subject to the restrictions that the unit cell be no larger than the one shown and further that each lattice site have the same distribution of parallel and antiparallel nearest and next-nearest neighbors. Ordering types of the first, second, and third kind have been named in analogy with the face-centered cubic lattice ordering schemes, i.e., ordering of a given kind has the same distribution of neighbors in both lattices. The hexagonal form of β-MnS was found to have ordering of the third kind. Hence it possesses exactly the same spin correlation as the cubic form of β-MnS, despite the fact that the magnetic ion structure has been changed. This is, however, in line with an indirect exchange coupling mechanism since both forms of β-MnS can be considered to be made up of regular Mn_4S tetrahedra and hence to involve similar $Mn-S-Mn$ bonds. The nearest and next-nearest neighbor configurations for all three forms of MnS are shown in Fig. 9. Figure 10 shows an alternative way of looking at the spin arrangements for the three forms based on the fact that in the rock salt and zinc blende structures the Mn^{++} ions are cubic close-packed while in the wurtzite structure they are hexagonal close-packed. In the cubic case the close-packed planes (111) are stacked in an *ABCABC*—repeat pattern. In the hexagonal case, the close-packed planes (001) are stacked *ABAB*—. Examination of the two β forms, both of which possess nearest neighbor coupling, shows that the close-packed planes have the same internal spin arrangement but that they are stacked in the two cases according to the requirements of either cubic or hexagonal close-packing.

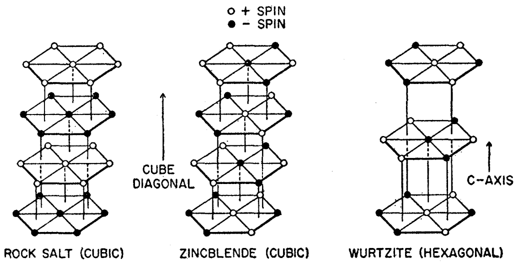


FIG. 10. Stacking of close-packed planes for the three forms of MnS.