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On the Ferromagnetism of CoS_2

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A neutron diffraction investigation of the ferromagnetic state of CoS_2 has been carried out in the course of a general study of the properties of transition metal chalcogenides and pnictides. CoS_2 crystallizes with the pyrite type structure [1-2] and its magnetic properties have previously been examined [3-7] by magnetic susceptibility and magnetization measurements.

The CoS_2 sample was prepared from a stoichiometric mixture of the components (99.999 % pure Co rod, Johnson, Matthey & Co., Ltd. and 99.999+ % pure S, American Smelting and Refining Co.) by heat treatment at 500°C for 7 days. After crushing, the sample was reannealed at 800, 700, and 600°C for 7 days, and at 400°C for 14 days and finally cooled slowly to room temperature over a period of 10 days. X-Ray diffraction data were obtained in a Guinier camera (80 mm diameter, monochromatized Cu$K\alpha_1$-radiation (λ = 1.54050 Å), and KCl as internal standard) at room temperature. A General Electric powder diffractometer with cryostat attachment (Cu$K\alpha$-radiation and diamond powder as internal standard) was used at liquid nitrogen temperature. Neutron diffraction data (neutron source JEEP I, λ = 1.148 Å) were collected at liquid helium, liquid nitrogen, and room temperature using a vanadium sample holder.

The lattice constant $a = 5.528 \pm 0.005$ Å obtained at room temperature is in agreement with the previous lattice constant values.[1,2,7,8] Since room temperature is higher than the Curie temperature of 110−116°K [5-7] reported for CoS_2, the structural parameter x of the S atoms could be checked by neutron diffraction data in the paramagnetic state of the compound. (The pyrite type crystal structure with space group $Pa3$ places 4Co in (a) and 8S in (c).) Least-squares refinement gave $x = 0.389$ with $R = \sum|jF_o^2 - jF_c^2| / \sum jF_o^2 = 0.055$ (*cf.* Table 1). This x-value is identical with the value ($x = 0.389 \pm 0.001$) found in the X-ray diffraction study of Elliott.[2] The nuclear scattering lengths $b_{Co} = 0.28 \times 10^{-12}$ cm and $b_S = 0.31 \times 10^{-12}$ cm listed in *International Tables* [9] were used in these calculations. Roth [10] (see also van Laar [11]) has suggested the considerably smaller value $b_{Co} = 0.232 \times 10^{-12}$ cm. Least-squares refinement based on this b_{Co}-value was also tried, and gave the result $x = 0.392$ and $R = 0.081$. However, thermal vibrations of unreasonable magnitudes were found in the last case and this result together with the higher R-value indicate that the former set of parameters is more correct than the latter. $b_{Co} = 0.28 \times 10^{-12}$ cm was accordingly used throughout the remainder of this study.

The form factor for Co^{2+} given by Scatturin *et al.*[12] was used to calculate F_{magn}^2-values. The comparison of jF_o^2 and jF_c^2 at 4.2°K (Table 1) gave good agreement ($R = 0.040$) for a ferromagnetic arrangement of the moments with spin quantum number $S_{Co} = 0.5 \pm 0.1$. This value agrees within the accuracy stated with $\mu_p = 1.85$ B.M. observed for the paramagnetic state of CoS_2 by Néel and Benoit [5] and Benoit [6] whereas it differs somewhat from $\mu_p = 2.17$ B.M. recently reported by Heidelberg *et al.*[7]

The powder neutron diffraction technique leaves the direction of the moments undetermined within the cubic unit cell, *cf.* Shirane.[13] It should be mentioned, however, that a slight broadening of the peak profiles for some of the reflections has been observed at 4.2°K indicating a deformation of the cubic symmetry. A crystallographic distortion below T_c is quite probable, but attempts to verify a deformation at 80°K by X-ray diffraction experiments were unsuccessful. Further experiments will be carried out in order to resolve this ambiguity, and

Table 1. Observed and calculated neutron diffraction data for CoS_2.

hkl	$T = 4.2°K$			$T = 298°K$		
	Type	jF_o^2	jF_c^2	Type	jF_o^2	jF_c^2
111	"N" + M	3.5	4.0	"N"	0.0	0.0
200	N + M	17.4	17.3	N	15.5	14.5
210	N	30.9	29.5	N	30.0	29.5
211	N	37.1	34.7	N	35.6	34.7
220	N + M	22.6	21.0	N	17.7	17.2
311	N + M	87.9	88.2	N	72.9	81.8
222	N + M	9.3	12.1	N	11.0	10.3
230	N	50.7	53.8	N	56.9	53.8
321	N	79.1	77.9	N	80.0	77.9

thus possibly also obtain information about the direction of the moments.

Although CoS_2 is reported to exhibit metallic conduction,[14] the general (8−N) rule (*cf.* Kjekshus [15]) appears to be satisfied for this compound. The formula CoS_2 gives $a = 2$, its crystal structure (showing S−S pairs with interatomic distance 2.12$_6$ Å) gives $P = 2$ and $Q = 0$, and the assumption of 2 valence electrons per Co and 6 per S give $n = 14$ and accordingly $(n + P - Q) = 8a$. The assumed number of 2 valence electrons per Co corresponds to a $t_{2g}^6 e_g^1$ configuration of localized electrons on the Co atoms which is consistent with $S_{Co} = 1/2$. With the electron configuration $t_{2g}^6 e_g^1$ on Co the Jahn-Teller effect should be operative in CoS_2 (in the paramagnetic state as well as the ferromagnetic), producing a distortion of the CoS_6 octahedra. The slight deformation of the octahedral angle from 90 to 86.0° in CoS_2 may indeed be sufficient to remove the degeneracy of the e_g orbitals, but it should be emphasized that octahedral angles in the range 84.4−86.9° are observed for all compounds with the pyrite type crystal structure.

Among the binary chalcogenides and pnictides of the sub-group elements, 28 are known to crystallize with the pyrite type crystal structure. CoS_2 here provides the only example of ferromagnetism. MnS_2, $MnSe_2$, and $MnTe_2$ show antiferromagnetic states,[16] whereas excepting $CoSe_2$, NiS_2, and $NiSe_2$ (which are presently being examined as a continuation of this study) the remaining compounds appear to exhibit diamagnetism. (The diamagnetic behavior can in most cases be attributed to a t_{2g}^6 configuration of localized electrons on the metal atoms.) The cooperative magnetic phenomena in these compounds are obviously not produced by a direct exchange interaction since the shortest interatomic metal-metal distance in the compounds with pyrite type crystal structure ranges from 3.821 to 4.909 Å (3.905 Å in CoS_2). An indirect type of exchange interaction (super-exchange (I, II) or virtual double-exchange, *cf.*, *e.g.*, Goodenough [17]) is accordingly operative. The reason for the antiferromagnetic coupling in MnS_2, $MnSe_2$, and $MnTe_2$ and the ferromagnetic coupling in CoS_2 can be easily explained on the basis of the semi-empirical rules for the ordering of magnetic moments (*cf.*, *e.g.*, Wollan [18] and Goodenough [17]). In the pyrite type crystal structure orbital overlap can occur between the e_g orbitals of the metal atoms and the p orbitals of the intervening non-metal atoms. The sign of the magnetic exchange interactions will according to the semi-empirical rules be determined by the population of the e_g orbitals. For MnS_2, $MnSe_2$, and $MnTe_2$ with $S_{Mn} = 5/2$ all d orbitals are half-filled ($t_{2g}^3 e_g^2$) and the magnetic coupling is necessarily antiferromagnetic. In CoS_2 with electron configuration $t_{2g}^6 e_g^1$ it is possible for an empty e_g orbital of one Co to overlap one end of an S 4p orbital and the other end of the same S 4p orbital to overlap a half-filled e_g orbital of another Co. The resulting magnetic coupling in CoS_2 will accordingly be ferromagnetic.

The molecular field theory (*cf.* Smart [19]) gives an exchange parameter J/k of 18.3 or 19.3°K on the basis of T_c-values reported to be 110 [5,6] or 116°K.[7] However, the simple molecular field theory requires a θ/T_c ratio of 1, which differs from the observed values 1.46 [5,6] and 1.32.[7] Improvement on the simple molecular field treatment is obtained by the various effective field approximations, of which *e.g.* the constant coupling approximation would predict $\theta/T_c = 1.22$ in the case of CoS_2. (It must be emphasized that the use of the constant coupling approximation leads to a considerable increase in the J/k-value. $J/k = 22.3$ or 23.5°K is obtained for $T_c =$ 110 or 116°K.)

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The Synthesis of 2-Carboxydibenzyl Selenide

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Unsubstituted and some alkyl-substituted five- and six-membered lactones have been studied by one of us [1,2] for the purpose of using these compounds as starting materials in the syntheses of the corresponding γ- and δ-selenosubstituted carboxylic acids. This was made possible through their reaction with sodium benzyl selenolate in a dimethyl formamide solution. In this way a simple and convenient method of syntheses was developed. Recently the investigation was extended and β-propiolactone was studied for the same purpose as above, and we found, as expected, that this very reactive compound gives an almost quantitative yield of β-selenosubstituted propionic acids with different types of reagents.[3]

It was also of interest for us to investigate if other substituents than alkyl groups in the five-membered lactone ring permit the reaction with sodium benzyl selenolate in a dimethyl formamide solution. A preliminary report on our results will be given in this paper.

In the present investigation, it was considered of importance to ascertain whether an amino group as substituent in the lactone ring permits the reaction with sodium benzyl selenolate. So far, we have had no chance to make any experiment with α-amino-γ-butyrolactone, because it has not been possible for us to isolate it. This was certainly caused by a reaction very similar to that one observed by Sudo,[4] who reports the rapid dimerization of α-amino-γ-butyrolactone into 3,6-(β-hydroxyethyl)-2,5-diketopiperazine. Our interest was thus directed towards the stable hydrobromide of the lactone in question, but in this case a too low solubility in dimethyl formamide prevented any reaction.

We have also made experiments with α-acetyl- and α-formyl-γ-butyrolactones, but also in these cases no reaction took place with sodium benzyl selenolate, because of decomposition of the lactones at the temperature necessary for the reaction.