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Structure and Magnetic Susceptibilities of $CoMo_2S_4$

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Received June 1, 1968

The structure of a new compound $CoMo_2S_4$ has been determined from X-ray powder diagrams. It is monoclinic with a deformed hexagonal close packing of the sulfur atoms and Co and Mo in octahedral surroundings. The short intermetallic distances indicate metal bonding. The magnetic susceptibilities were measured from 120 to 1000°K; above 350°K a magnetic moment of one unpaired electron was deduced.

Introduction

A series of ternary chalcogenides of the first transition row with the composition $M'M_2X_4$ (M' = Ni, Co; M = Cr, V) have been described in the literature.[1,2,3] They have a monoclinic type of structure. The possibility of intermetallic bonding was put forward in attempts to interpret some of their physical and structural properties.

We have investigated combinations of the first- and second-row transition elements. This study revealed the existence of a compound $CoMo_2S_4$, isomorphous with the above-mentioned series. We determined its structure and measured the magnetic susceptibilities.

Experimental Section

The compound was prepared by heating the elements in evacuated silica tubes at 1000°C for ten hours; the sample was powdered and heated again for three days at 1100°C. A small excess of cobalt metal was invariably found in the composition $Co_{x=1}Mo_2S_4$, so that the cobalt concentration in the actual compound must be slightly lower than $x = 1$. The X-ray diffraction experiments were carried out on a Philips X-ray powder diffractometer. The material showed preferred orientation to an extremely high degree. This could be considerably reduced by carefully mixing the sample with Canada balsam[4] and using a rotating sample holder on the diffractometer.

The magnetic susceptibilities were measured in the temperature range 120-1000°K with the aid of the Faraday balance. We did not measure the powder $Co_xMo_2S_4$ ($x \sim 1$) because it proved impossible to obtain samples that were free from ferromagnetic cobalt. By varying the amount of sulfur and cobalt, we found that the samples Co_xMoS_2 with $x = 0.1$–0.4 in particular were amenable to measurement; they contained an excess of MoS_2, which is diamagnetic. For the very small traces of Co that still remained after this procedure, corrections were applied.

Results

Determination of the Structure. The powder diagram was indexed on a monoclinic lattice with cell parameters $a = 5.895 \pm 0.001$ Å, $b = 3.276 \pm 0.000$ Å, $c = 11.47 \pm 0.001$ Å, and $\beta = 92.174 \pm 0.004$; the space group is assumed to be $I2/m$. The structure was roughly determined from diffractograms. Because of the numerous overlaps only 21 out of 80 reflections could be measured accurately. The refinement was started with the ideal positions used in the refinement of the isomorphous compound Cr_3S_4.[5] The final positions are as follows.

Table I. Atomic positions

	x	z
2 Co in (2a)	0	0
4 Mo in (4i)	-0.051 ± 0.005	0.259 ± 0.003
4 S_I in (4i)	0.333	0.895 ± 0.007
4 S_{II} in (4i)	0.333	0.368 ± 0.007

The final R value based on the 21 structure factors is 11.8% (Table II). The R value based on the intensities for all reflections observed is 30%. Considering the quality of intensity data (influenced by preferred orientation) and their limited quantity, it would be useless to introduce a temperature factor and possible lower symmetries of the space group. For the same reason a refinement of the x parameters of sulfur was unsuccessful.

Magnetic Measurements. We measured the susceptibilities of three different samples, *viz.* $Co_{0.1}MoS_2$, $Co_{0.2}MoS_2$, and $Co_{0.33}MoS_2$. The values of χ plotted against the reciprocal temperature T^{-1} showed a linear behaviour above ~ 350°K (Figure 1), pointing to a paramagnetic Curie-Weiss behaviour described by the

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(1) R. J. Bouchard, W. T. Robinson, and A. Wold, *Inorganic Chemistry*, *5*, 977 (1966).
(2) R. J. Bouchard and A. Wold, *J. Phys. Chem. Solids*, *27*, 591 (1966).
(3) S. L. Holt, R. J. Bouchard, and A. Wold, *J. Phys. Chem. Solids*, *27*, 755 (1966).
(4) J. M. van den Berg, *J. Less-Common Metals*, *13*, 363 (1967).
(5) F. Jellinek, *Acta Cryst.*, *10*, 620 (1957).

Table II. Observed and calculated structure factors used in the refinement

h k l	$\lvert F_o\rvert$	$\lvert F_c\rvert$	h k l	$\lvert F_o\rvert$	$\lvert F_c\rvert$
0 0 2	284	281	$\bar{3}$ 0 1	210	168
1 0 1	198	213	0 0 6	385	251
$\bar{1}$ 0 3	272	229	$\bar{3}$ 0 3	360	386
2 0 0	283	274	3 1 0	559	606
0 1 3	242	294	$\bar{1}$ 0 7	437	339
2 1 1	339	394	$\bar{3}$ 0 5	264	219
1 0 5	222	194	2 2 2	336	411
$\bar{2}$ 0 4	435	433	$\bar{4}$ 1 1	270	233
$\bar{1}$ 1 4	611	616	$\bar{3}$ 2 3	370	389
2 0 4	572	451	5 0 1	234	262
1 1 4	762	753	$\bar{2}$ 2 6	229	210

formula

$$\chi_M = \frac{C_M}{T-\theta} + A_M$$

with a rather large temperature-independent term A_M (extrapolation to $T^{-1}=0$) and possibly a non-zero value of θ. This description did not hold good at all when one or more χ values measured below 350°K were included in the calculation. Below this temperature χ shows a much less temperature-dependent behaviour. There is a rather abrupt change at 350°K. The results of a least-squares calculation for χ values above 350°K are listed in Table III.

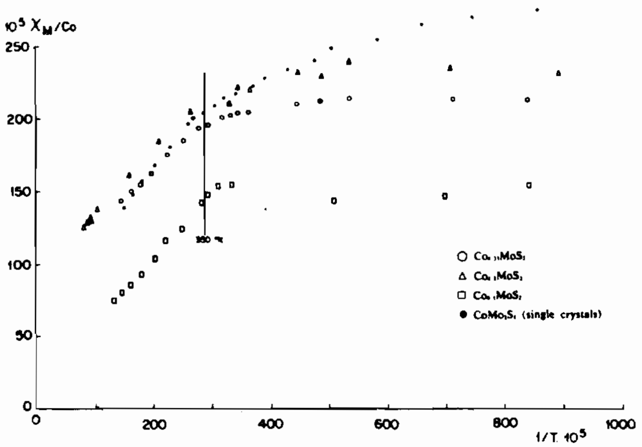

Figure 1 . Magnetic susceptibilities *vs.* reciprocal temperature.

somewhat higher value of A_M than expected; this may be due to the fact that $Co_{0.33}MoS_2$ and $Co_{0.1}MoS_2$ were corrected for the field dependence caused by traces of ferromagnetic cobalt, whereas the χ values of $Co_{0.2}MoS_2$ showed no field dependence and did not need any correction. The X-ray diagrams revealed the $CoMo_2S_4$ and MoS_2 phases only.

The transition at 350°K was carefully checked by means of Guinier photographs, taken at temperatures varying from 295°K to 500°K. Only a slight expansion of the lattice and no change of structure were observed. Nor could a transition be detected by differential thermal analysis.

Meanwhile single crystals of $CoMo_2S_4$ have been isolated. The magnetic susceptibilities showed roughly the same behaviour; the parameters above 350°K are listed in Table III.

Discussion

Structure. A projection of the structure is shown in Figure 2. The sulfur atoms have a deformed hexagonal close packing with one layer ($\perp$ c axis) of octahedral holes completely occupied by molybdenum, the next one half occupied by cobalt. From the refinement* it appears that the molybdenum cations in the planes (0 0 ¼) and (0 0 ¾) are shifted from the ideal positions in such a way that zigzag chains of molybdenum ions are formed parallel to the b axis.

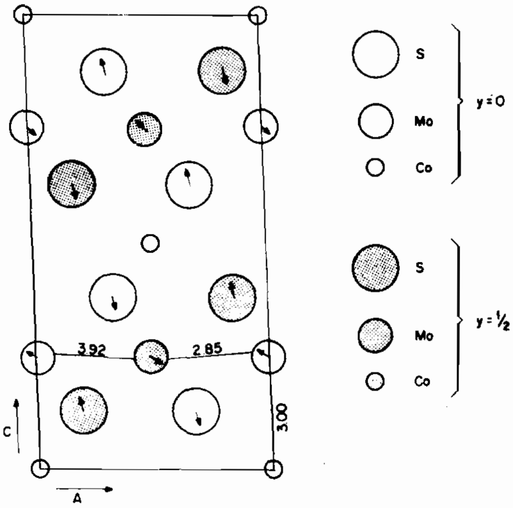

Figure 2. Projection of unit cell of $CoMo_2S_4$ along b axis. Arrows indicate deviations from ideal positions.

Table III. Magnetic parameters

	A_M	C_M	θ	μ (μ_B)
$CoMo_2S_4+8MoS_2$ (x=0.1)	0.205 (0.020)×10^{-3}	0.392 (0.009)	+33 (8)	1.77
$CoMo_2S_4+3MoS_2$ (x=0.2)	0.893 (0.012)×10^{-3}	0.549 (0.010)	−74 (10)	2.10
$CoMo_2S_4+MoS_2$ (x=0.33)	0.764 (0.024)×10^{-3}	0.520 (0.014)	−84 (10)	2.04
$CoMo_2S_4$ (single crystals)	0.589 (0.015)×10^{-3}	0.536 (0.008)	− 5 (6)	2.00

The calculated constants for $Co_{0.1}MoS_2$ are not quite reliable because of the low concentration of $CoMo_2S_4$. The much lower value of A_M (~0.205×10^{-3}) reflects the presence of a much larger concentration of MoS_2 ($\chi_{dia}=0.077\times10^{-3}$) and its difference (7 MoS_2) from the value of A_M for x=0.33 bears this out. On the other hand $Co_{0.2}MoS_2$ has a

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(*) A refinement based on single-crystal intensities confirmed our analysis and will be published elsewhere.

The distances within and between the chains are 2.85 Å and 3.92 Å, respectively. The occurrence of chains of molybdenum ions points to a strong intermetallic bonding between these ions. In addition, the rather short distance of 3.00 Å between Co and Mo indicates some interaction between the two and is comparable to the distances in $Co_{1/3}NbS_2$.[6] $CoMo_2S_4$ is comparable to the compounds Mo_2S_3, Re_3P_4,[7] NiV_2S_4, and NiV_2Se_4 [1] in that zigzag chains with short distances are formed. In this respect these compounds differ from Cr_3S_4 and $NiCr_2S_4$ which provide no indication for metal-metal bonding.[1,2,3] The short Mo–Mo distance of 2.85 Å is also comparable to the Mo–Mo bond length of 2.89 Å in the sulfur-bridged dimeric complex $[C_6H_5MoO]_2S_2$, which is diamagnetic.[8] The distances are listed in Table IV.

Table IV. Interatomic distances

Co–Co	3.28	S_I-S_I	3.28	3.28	3.55
Mo–Mo	3.28	$S_{II}-S_{II}$	3.28	3.05	3.80
Co–Mo	3.00	S_I-S_{II}	3.40	3.66	3.35
Mo–Mo	2.85				
Mo–Mo	3.92	around S_I			
Co–S_I	2.41	2S–Co	2.41		
Co–S_{II}	2.34	2S–Mo	2.57		
Mo–S_I	2.55	1S–Mo	2.55		
Mo–S_I	2.57				
Mo–S_{II}	2.38	around S_{II}			
Mo–S_{II}	2.38	1S–Co	2.34		
Mo–S_{II}		2S–Mo	2.38		
		1S–Mo	2.38		

Magnetism. The approximation used for the description of the magnetic behaviour above 350°K results in a magnetic moment corresponding to one unpaired electron. As the molybdenum atoms show a strong tendency to intermetallic bonding, it seems reasonable to assume that their d electrons are all in a metallic t_2 band, comparable to that in Mo_2S_3 which is a metallic conductor.[9] Assuming the formal valence state to be $Co^{2+}Mo_2^{3+}S_4^{2-}$, the one unpaired electron is localized on Co^{2+} in an e_g level of the low-spin state d^7.

Although a moment of one unpaired electron can reasonably be expected, this approximation does result in a temperature-independent term A_M of 0.7 to 1.1×10^{-3} (corrected for diamagnetism), which seems too high to be attributed only to delocalized electrons in narrow d bands. It is noteworthy that a term A_M of approximately equal magnitude has been derived for $CoNb_3S_6$,[6] which also showed a moment corresponding to low-spin Co^{2+}. In the meantime, however, we succeeded in obtaining very pure crystalline material of $CoNb_3S_6$ by means of iodine vapour transport.* For this sample the term A_M worked out at a much lower and acceptable value, *viz.* approximately zero, and we found a magnetic moment of two unpaired electrons. In the powder sample the Néel temperatures of traces of cobalt oxides or sulfides most probably influence the slope of the χ curve and consequently the values of A_M and C_M. However, such a marked change of A_M is not observed for the single crystals of $CoMo_2S_4$.

Assuming the observed temperature dependence to be a characteristic of $CoMo_2S_4$, we may attribute the abrupt change at 350°K to an antiferromagnetic transition, although the calculated value of $|\theta|$ is relatively low. Alternatively, the behaviour below 350°K could be described as metallic Pauli paramagnetism. An argument in support of this is provided by the linear dependence on T^2 found for $Co_{0.33}MoS_2$.

In this connection it is of interest to consider the compounds Co_3S_4 and $CoNi_2S_4$ which are metallic conductors.[12] They show that for tetrahedrally surrounded Co^{2+} the σ-bonding t_{2g} orbitals and for octahedrally surrounded Ni^{3+} the σ-bonding e_g orbitals are broadened to a band;[13] on the other hand in CoS the Co^{2+} ion in octahedral surroundings shows a localized magnetic moment of one unpaired electron and in the spinel compound $CoRh_2S_4$, which has a moment corresponding to three unpaired electrons, the Co^{2+} ion is in the high-spin state.[10] Further experiments are in progress to check this transition and to find out which is the true interpretation.

Acknowledgments. The author wishes to thank Miss M. Burink and Miss M. van Diepen for their assistance in the X-ray analysis and the measurement of the magnetic susceptibilities. Thanks are also due to Mr. J. N. Helle, who prepared the single crystals.

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