ACTA CHEMICA SCANDINAVICA 23 (1969) 2325–2334

On the Magnetic Properties of $CoSe_2$, NiS_2, and $NiSe_2$

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Polycrystalline samples of $CoSe_2$, NiS_2, and $NiSe_2$ have been studied by X-ray and neutron diffraction, and magnetic susceptibility measurements between 4 and ~900°K. The compounds are found to have the pyrite type crystal structure throughout this temperature range, and refined values are presented for the positional parameters of the chalcogen atoms at room temperature. None of the compounds show any evidence of magnetic ordering at 4°K. $CoSe_2$ and NiS_2 exhibit temperature dependent paramagnetism of the Curie-Weiss law type, corresponding to one and two unpaired electrons per metal atom, respectively, whereas $NiSe_2$ shows weak paramagnetism associated with a delocalized electron configuration. Anomalies in the linear thermal expansion curves for $CoSe_2$ and NiS_2 at ~475 and ~440°K, respectively, correspond to anomalies in the temperature dependence of their magnetic susceptibilities. The origin of the anomalies is attributed to changes in the anharmonic vibrations of the lattices at these temperatures.

The existence of some 50 binary compounds (and a large number of ternary phases) with the FeS_2-*p* (*p*=pyrite) type crystal structure is reported in the literature. Some members of this class of compounds occur in nature as minerals, but most of them have been prepared synthetically. Notably, a considerable number of previously unknown compounds with this type of structure have recently been synthesized by the high temperature high pressure technique.[1–7] The FeS_2-*p* type structure is most frequently found among the chalcogenides and pnictides of the subgroup elements, but examples like NaO_2,[8] CaC_2(?),[9] CdO_2,[10] and SiP_2[1] show that its occurrence is not limited to such metal components. The FeS_2-*p* type structure may in fact prove to be much more widespread than previously anticipated.

The chemical and physical properties show, as expected, considerable variations within such a large group of compounds. Although most of these compounds have the stoichiometric 1:2 composition, some notable exceptions

exhibit homogeneity ranges and/or non-stoichiometric formulae. Their electrical conductivities range from ionic- or semiconducting (*e.g.* MnS_2[11]) to very good metallic conduction (*e.g.* $AuSb_2$[12]), and transitions to the superconducting state have been observed for some of the compounds (*e.g.* $Ir_{0.67}Te_2$[13]). Different types of magnetism have also been revealed among the compounds with the FeS_2-*p* type structure, for example diamagnetism (*e.g.* RuS_2[14]), temperature independent paramagnetism (*e.g.* $CuSe_2$[2]), Curie-Weiss type of temperature dependent paramagnetism (*e.g.* $MnTe_2$ above T_N[15]), ferromagnetism (*e.g.* CoS_2 below T_C[16–18]), and antiferromagnetism (*e.g.* $MnTe_2$ below T_N[15]). The above examples have been limited to well established cases, and although further definite examples could be given, there are a considerable number of cases for which lacking or ambiguous data exclude reliable interpretations.

The present paper concerns the magnetic properties of $CoSe_2$, NiS_2, and $NiSe_2$, which despite having been extensively studied[7,16,19–24] are still not understood in detail, in particular in relation to the electrical properties.[7,23–30] The FeS_2-*p* type crystal structure of these compounds is unequivocally established,[7,21–23,31–33] but some uncertainties exist concerning the values of the structural parameters of the chalcogen atoms.

MATERIALS AND METHODS

The pure elements used in this study were 99.999 % Co and Ni (Johnson, Matthey & Co., Ltd.; turnings from rods), 99.999+ % S (American Smelting and Refining Co.), and 99.998 % Se (Bolidens Gruvaktiebolag, Sweden). The samples were prepared by heating weighed quantities of the components (in the stoichiometric 1:2 ratio) in evacuated and sealed silica tubes. During the syntheses, the temperature was slowly increased to 500°C in the case of NiS_2 and 700°C for $CoSe_2$ and $NiSe_2$, the samples were kept at these temperatures for 7 days, and then cooled slowly to room temperature. The samples were afterwards subjected to crushing and three further reannealings (with intermediate crushings) at temperatures between 800 and 400°C. The opening of the capsules for crushing of the samples during the annealing processes was found to be essential in order to avoid non-equilibrium states which otherwise appear to result from the kinetics of the reactions. The temperature of the furnaces was kept constant to within ± 0.5°C, using Getrosist (Philips) temperature regulators in combination with a Frigistor reference chamber for the cold points of the Pt/Pt−Rh thermocouples. In order to minimize the effect of thermal gradients in the furnaces, the silica capsules were kept as short as possible and surrounded by quartz sand.

X-Ray powder photographs were taken in a Guinier type camera of 80 mm diameter with monochromatized Cu$K\alpha_1$-radiation ($\lambda = 1.54050$ Å) using KCl as internal standard. A General Electric powder diffractometer with cryostat attachment (Cu$K\alpha$-radiation and diamond powder as internal standard) was used to collect X-ray data below room temperature. High temperature X-ray powder photographs were obtained in a 190 mm diameter Unicam camera with the samples sealed in thin-walled quartz capillaries. The temperature of the furnace surrounding the specimen was kept constant to within ± 5°C during the exposures. The Pt/Pt−Rh thermocouples of the furnace had been calibrated with a standard couple located at the position of the specimen. In the latter case, lattice dimensions were determined from the high-angle reflections, utilizing the Nelson-Riley[39] type extrapolation.

The magnetic susceptibilities of the samples were measured between 90 and 950°K by the Faraday method (maximum field ~8000 Ø) using 40−150 mg samples.

Powder neutron diffraction data were collected at liquid helium, liquid nitrogen, and room temperatures, using cylindrical sample holders of aluminium or vanadium. Neutrons of wavelengths 1.148 to 1.864 Å were obtained from the reactors JEEP I and JEEP II. The integrated intensities from the neutron diffraction diagrams were converted

to jF_o^2 by multiplication with L^{-1}. For the calculation of F_c^2-values, the nuclear scattering lengths were taken as $b_{Co}=0.28\times10^{-12}$ cm, $b_{Ni}=1.03\times10^{-12}$ cm, $b_S=0.31\times10^{-12}$ cm, and $b_{Se}=0.89\times10^{-12}$ cm, and allowance was made for isotropic temperature factors.

RESULTS AND DISCUSSION

(i) *Crystal structure.* The room temperature values of the lattice constants determined by the Guinier, Debye-Scherrer, and neutron diffraction techniques agree within the estimated error limits, and the data listed in Table 1 are also reasonably consistent with those reported in the literature.[7,21,22,29,31–38]

Table 1. Structural data for $CoSe_2$, NiS_2, and $NiSe_2$. (Lengths in Å and angles in °.)

Compound	$CoSe_2$	NiS_2	$NiSe_2$
a	5.8593 ± 0.0005 (20 ± 1°C)	5.6873 ± 0.0005 (20 ± 1°C)	5.9629 ± 0.0007 (20 ± 2°C)
x	0.3795 ± 0.0016	0.3955 ± 0.0016	0.3830 ± 0.0012
$M-X(6)$[a]	2.438 ± 0.003	2.401 ± 0.004	2.488 ± 0.003
$X-X(1)$[a]	2.446 ± 0.032	2.059 ± 0.032	2.417 ± 0.025
$M-X$[b]	3.770 ± 0.012	3.539 ± 0.012	3.809 ± 0.009
$X-X$[b]	3.299 ± 0.010	3.290 ± 0.010	3.377 ± 0.008
$M-M$[b]	4.143	4.022	4.126
$M-X-M(3)$	116.4 ± 0.2	113.7 ± 0.2	115.7 ± 0.2
$X-X-M(3)$	101.1 ± 0.4	104.8 ± 0.4	101.9 ± 0.3
$X-M-X(6)$	85.2 ± 0.1	86.5 ± 0.1	85.5 ± 0.1

[a] Bonding interatomic distances.
[b] Shortest interatomic distances neglected as bonding.

The neutron diffraction data for $CoSe_2$, NiS_2, and $NiSe_2$ collected at room temperature (Table 2) show no evidence of magnetic contributions to the reflections, and since these data can be considered to be rather accurate, it was decided to utilize them for redeterminations of the structural parameter of the chalcogen atom in the three compounds. In terms of space group $Pa3$ the FeS_2-p type crystal structure has respectively four metal and eight non-metal atoms in the positions 4(a) and 8(c), the latter position containing one variable parameter x.

Despite the fact that the refinement of essentially one parameter is required for this structure type, the use of the method of least squares is unfavourable due to the relatively small number of observations accessible for such calculations. It was therefore decided to perform refinements by comparisons of the values of the reliability index $R=\sum|jF_c^2-jF_c^2|/\sum jF_o^2$ for different x in the range $0.370\leqq x\leqq0.405$, while varying also the thermal parameters. In the

Table 2. Observed and calculated neutron diffraction data for $CoSe_2$, NiS_2, and $NiSe_2$.

hkl	$CoSe_2$			NiS_2			$NiSe_2$		
	jF_o^2 4°K	jF_o^2 298°K	jF_c^2	jF_o^2 4°K	jF_o^2 298°K	jF_c^2	jF_o^2 4°K	jF_o^2 298°K	jF_c^2
111	21.4	22.2	20.83	67.8	77.9	66.71	23	16.2	11.80
200	11.8	14.0	13.91	128.0	137.8	135.48	152	138.5	140.24
210	275.8	277.0	286.06	25.6	24.3	25.72	253	242.2	270.88
211	317.5[a]	301.9	302.23	26.8[a]	31.5[a]	32.27	293	265.8	298.07
220	—[a,b]	19.1	15.67	221.8[a]	213.7[a]	219.92	240	232.0	210.85
221	0	0	1.83	0	0	3.33	0[a]	0[a]	5.46
311	295.6	299.4	301.56	531.2	530.4	535.69	982	976.2	996.11
222	0	11.5	10.06	145.8	139.2	138.51	159	138.0	136.27
230	334.4	346.8	354.38	56.7	58.6	58.60	363	375.1	390.54
321	622.2[c]	621.5[c]	612.18	70.6[c]	79.6[c]	81.29	674[c]	611.8[c]	620.16
400	225.4[a]	216.0	212.74		27.1[a]	23.10	0	60.3[b]	48.96
410; 322		0[c]	5.92		0[c]	14.28	0[c]	0[c]	18.78
411		0	3.86		0	8.38	0	0	12.01
331		30.4[a,b]	25.49		347.9	350.87	218	167.6	122.99
420		14.0[a,b]	12.45		305.6	305.91	296	321.9	280.68
421		511.3[a–c]	564.85				465[c]	513.6[c]	520.38
332		260.7[a,b]	294.55				280	276.5	274.54
422							~500[a,b]	~500[a,b]	393.61
430							0	0	15.74
431							0[c]	0[c]	24.99
511; 333							1579[c]	1598.2[c]	1598.25
250; 432							801[c]	903.5[c]	905.98

[a] Overlapped by Al-reflection.
[b] Not included in the calculation of R, mostly due to uncertain background.
[c] Overlapping of reflections with equal $h^2+k^2+l^2$, but different F_c.

final calculations constant B-values were chosen in order to simplify the process, and this furthermore allows a graphical representation of the results.

A pronounced minimum in $R(x)$ is found for each of the three compounds, $R(x)$ increasing monotonically on both sides of this minimum throughout the examined range of x. The relevant portions of the $R(x)$-curves near these minima are reproduced in Fig. 1. In accordance with convention the positions of the minima give the most probable values of x (see Table 1). The accuracy of the determination of x according to this method is related to the shape of the $R(x)$-curve in the vicinity of the minimum, but it is difficult to give an objective criterion for reliable estimation of the error limits.

There is a degree of relationship between the weighted reliability index ($R' = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{\frac{1}{2}}$ where w denotes the weight factor) and that used in the present study (*vide supra*), but the noteworthy differences are sufficiently important to render substitution of the latter for the former in Hamilton's [40] significance test of somewhat doubtful validity. However, if this test is nevertheless used to estimate the accuracies in the determined x-values in relation to the $R(x)$-curves in Fig. 1, the error limits stated in Table 1 are obtained at a significance level of 0.01. Despite the justifiable doubts one may attach to the usefulness of this way of deriving the error limit, the deduced values are probably realistic estimates of the reliability of the determined parameters.

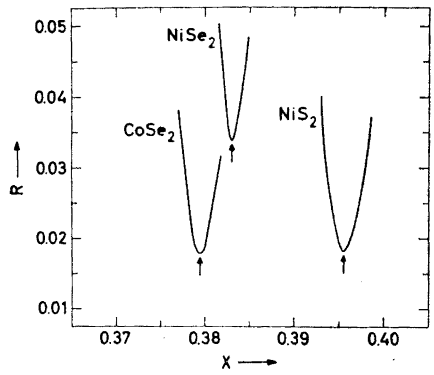

Fig. 1. The reliability index R as a function of the positional parameter x of the chalcogen atoms in the crystal structures of $CoSe_2$, NiS_2, and $NiSe_2$.

The x-parameters listed in Table 1 agree rather well with those reported in the literature.[21,22,31,32,34,35,38] This seems somewhat remarkable since none of the previous values (excepting that for NiS_2 by Elliott [38]) appear to have been obtained by systematic refinements. Some of the most important interatomic distances and angles are calculated on the basis of the presently revised data and are included in Table 1.

(ii) *Thermal expansion.* Anomalies in the temperature dependences of the magnetic susceptibilities of $CoSe_2$ and NiS_2 (see section iii) have occasioned X-ray examinations of all three compounds in the range 4—~800°K. Throughout this temperature range there is no indication of changes in lattice symmetry for any of the compounds and the essentially invariable relative intensities of the reflections confirm that the x-parameters in Table 1 are approximately independent of temperature. Since furthermore only insignificant differences occur in the temperature dependences of the profiles of the reflections, it can be concluded that the crystalline perfection of the samples remains very nearly unchanged, and that no drastic alterations take place in the harmonic components of the lattice vibrations.

The thermal expansion, which originates from the anharmonic terms in the potential energy of the interatomic displacements, shows distinct anomalies for $CoSe_2$ and NiS_2 (Fig. 2). The expansion curves are linear over considerable spans of temperature on both sides of the irregularities and for the lack of better criteria, the whole of the intermediate, non-linear regions are used to define the temperatures of the anomalies. The central points of the anomalous temperature regions (410—530°K for $CoSe_2$ and 420—450°K for NiS_2) are marked A and B on Fig. 2 and these temperatures coincide with those of the corresponding points on Fig. 3.

Although the anomalies are accentuated in the expansion curves, the major parts of the vibration spectra of the two lattices (*i.e.* the harmonic terms and probably most of the anharmonic) are unaffected by the occurrence of these phenomena. Consistent with this fact, no evidence of the anomalies could be detected by differential thermal analysis. (The three compounds were subjected to DTA between 20 and ~600°C, but the results gave no indication of transformations or anomalies in this range.)

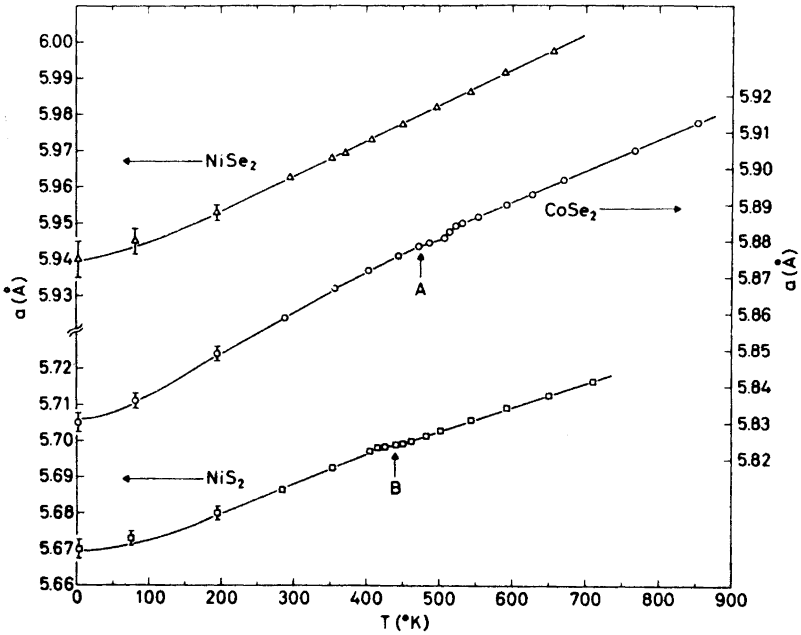

Fig. 2. The temperature dependence of the a-axis for $CoSe_2$, NiS_2, and $NiSe_2$. The vertical bars represent the uncertainty when the calculated error limits exceed the size of the symbols.

The linear expansion coefficient between the temperatures T and T' is $(a_T - a_{T'})/a_{293}(T - T')$ relative to the room temperature value of the lattice constant (a_{293}). The linear expansion coefficients for $CoSe_2$ are $19.6 \times 10^{-6}°K^{-1}$ (100—410°K) and $14.5 \times 10^{-6}°K^{-1}$ (530—850°K), for NiS_2 $15.8 \times 10^{-6}°K^{-1}$ (200—420°K) and $11.4 \times 10^{-6}°K^{-1}$ (450—710°K), and for $NiSe_2$ $16.4 \times 10^{-6}°K^{-1}$ (200—670°K). Due to the cubic symmetry, the thermal expansion coefficient of the interatomic distances equals (provided x is constant) that for the a-axis, and the volume expansion coefficient is three times that of the linear.

(iii) *Magnetic susceptibility.* The reciprocal magnetic susceptibility *versus* temperature curves for $CoSe_2$, NiS_2, and $NiSe_2$ are shown in Fig. 3.

Several samples of each compound were measured, excellent reproducibility generally being obtained whenever repeated measurements were performed on the *same* sample. However, it should be noted that heating of $NiSe_2$ above ~900°K during the measurements may change (depending on the actual temperature and/or the duration of the heat treatment) its thermo-magnetic curve shown in Fig. 3 considerably. This is attributed to the onset of thermal decomposition of $NiSe_2$ above this temperature. Excellent reproducibility has also been found between the *various* samples of $CoSe_2$ and NiS_2, respectively. In the case of $NiSe_2$ a (smaller) degree of irreproducibility between different samples over the temperature range 90—~700°K was detected. The likely explanation for this seems to be that the $NiSe_2$-samples are slightly inhomogeneous, *e.g.* resulting from composition variations within the homogeneity range $NiSe_{1.975}$—$NiSe_{2.000}$.[22]

Field strength dependent susceptibilities were not observed for any of the compounds and the results shown in Fig. 3 represent mean values obtained at several different

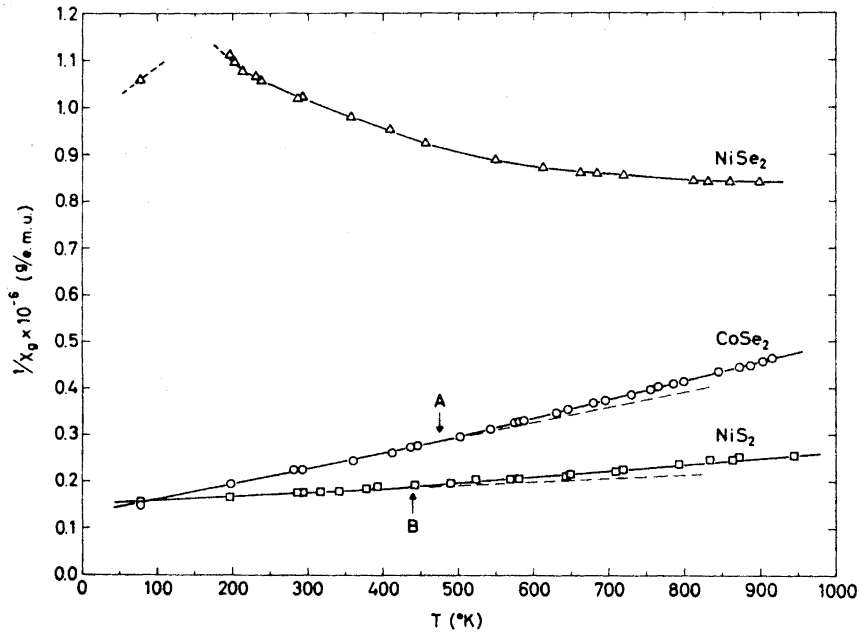

Fig. 3. The reciprocal magnetic susceptibility of $CoSe_2$, NiS_2, and $NiSe_2$ as a function of temperature.

field strengths. The experimental curves have not been corrected for induced diamagnetism. Lack of knowledge about the chemical bonding in these compounds makes it difficult to give reliable estimates of the correction terms, but according to the empirically deduced [41,42] core contributions for Co^{2+}, Ni^{2+}, S^{2-}, and Se^{2-} the limiting corrections may amount to -0.52×10^{-6}, -0.67×10^{-6} and -0.52×10^{-6} e.m.u./g for $CoSe_2$, NiS_2, and $NiSe_2$, respectively.

The thermo-magnetic data for $NiSe_2$ (Fig. 3; see also Refs. 7, 22, 23) suggest very strongly that no unpaired *d*-electrons are localized on the Ni atoms and the paramagnetism must consequently be attributed to delocalized electrons contained in incompletely filled band(s), *i.e.* consistent with its metallic type of conductivity.[7,23,25,28,30]

The $1/\chi$ *versus* T curves for $CoSe_2$ and NiS_2 shown in Fig. 3 are of the same form in that they both consist of two intersecting straight lines, the discontinuities of slope occurring at the points A and B in the diagram. The lower and higher temperature sections of the curves are consistent with an analytical description of the Curie-Weiss law type, *i.e.* $\chi^{-1}=C^{-1}(T-\theta)$. The interpretation of these results in terms of current theory falls naturally into three parts:

(1) The discontinuities of slope of the $\chi^{-1}(T)$-curves at $T_A=475\pm30$°K and $T_B=440\pm40$°K for $CoSe_2$ and NiS_2, respectively, occur at the same temperatures as the anomalies in the thermal expansion curves (see section ii). A corresponding anomaly has also been observed [7,24,25] at ~420°K in the temperature dependence of the electrical resistivity of NiS_2, although it

must be emphasized that this has previously [7,25] been interpreted as a transformation between extrinsic and intrinsic conduction mechanisms. An analogous situation has furthermore been reported [7,18,24] for the electrical resistivity, magnetic susceptibility, and thermal expansion data for CoS_2, the temperature of the anomaly being in this case ~400°K.

The most apparent inference, that transformations involving ordering of magnetic moments (corresponding to one and two unpaired electrons, respectively) occur at T_A and T_B is, however, inadmissable in view of the negligible ordered moment found for $CoSe_2$ and NiS_2 at 4°K by neutron diffraction (see section iv).

One concludes therefore that the anomalies in the magnetic susceptibilities of $CoSe_2$ and NiS_2 are coupled with changes in the anharmonic vibration spectra of the lattices. (It must be emphasized, however, that the lack of a more fundamental understanding of phenomena of this kind renders the choice between what is cause and what is effect somewhat arbitrary.)

(2) Consideration of the slopes (C^{-1}) of the $\chi^{-1}(T)$-curves on either side of the anomalies leads to magnetic moments ($\mu=\sqrt{8C}$) of 2.30 ± 0.05 and 2.05 ± 0.03 B.M./Co atom for $T<T_A$ and $T>T_A$, respectively, in the case of $CoSe_2$ and 3.15 ± 0.08 and 2.70 ± 0.08 B.M./Ni atom for $T<T_B$ and $T>T_B$, respectively, for NiS_2. These μ-values are reasonably consistent with most of those given in the literature,[7,16,19–21,23,24] taking into account the fact that only single μ-values, valid over the entire temperature range for each compound, are reported in the previous studies. With the exception of the μ-value found for NiS_2 above T_B, the above figures exceed those of 1.73 and 2.83 B.M. per metal atom predicted for $S=\frac{1}{2}$ and 1, respectively, using the "spin only" approximation ($\mu=g\sqrt{S(S+1)}$) with $g=2$. However, these discrepancies may easily be accounted for by assuming incomplete quenching of the orbital momenta. In order to preserve the "spin only" approximation, the residual orbital contributions due to spin-orbit coupling are conveniently taken into account by allowing increased values of g (*cf.* Jarrett *et al.*[24]).

According to the schematic energy diagram for the electronic band structure of $CoSe_2$ and NiS_2 proposed by Bither *et al.*[7] (see also Jarrett *et al.*[24]) the e_g electrons, *i.e.* those contributing to μ, are contained in a split sub-band which can accommodate only electrons with, say, spin-up states. This virtual e_g band is assumed to constitute the (incompletely filled) conduction band for $CoSe_2$ and the (completely filled) valence band for NiS_2, and although their widths are unspecified, these bands are considered to be narrow enough for the electrons to be polarized in one of the spin directions. The supposition of an e_g band (as opposed to the essentially localized energy levels implicitly assumed in the above considerations) leads to a degree of delocalization of the unpaired electrons and this itineracy (if significant) may in principle provide the basis for an alternative interpretation of the $\chi^{-1}(T)$-curves, *e.g.* in terms of their slopes, and thus also the μ-values. Since the hypothetical electronic band schemes for $CoSe_2$ and NiS_2 must necessarily lack the relevant details needed for estimation of magnetic parameters, further consideration of this model is excluded.

For $NiSe_2$ (*vide supra*) Bither *et al.*[7] suggest that the partially overlapping valence and conduction bands have both a virtual e_g character. If this simple model is valid, it ought to be possible to utilize the temperature dependence of χ (Fig. 3) for an analysis of the various contributions to χ from the core, Van Vleck, Landau-Peierls, and Pauli terms, when NMR Knight shift data as function of temperature become available (*cf.* Adachi *et al.*[23]). In this case it may therefore be possible to perform a fairly simple test of the usefulness of the proposed band scheme.

Regardless of the above considerations, it can apparently be safely concluded that the number of unpaired electrons in $CoSe_2$ and NiS_2 are, respectively, one and two per metal atom.

Consistent with the above explanation of the anomalies in the $\chi^{-1}(T)$-curves, the increased μ-value below T_A and T_B should also be attributed to variations in the spin-orbit couplings arising from crystal field effects, which, in turn, are associated with the changes in the anharmonic vibration spectra of the lattices.

(3) The deduced values of the Weiss constant $\theta = -380 \pm 50$ and -210 ± 50°K for $T < T_A$ and $T > T_A$, respectively, in the case of $CoSe_2$ and -2100 ± 300 and -1000 ± 200°K for $T < T_B$ and $T > T_B$, respectively, for NiS_2 are anomalously large in view of the lack of magnetic ordering at low temperatures. (With a reservation for the fact that the present study gives two θ-values for each compound, these values concur reasonably well with most of those found in the literature.[7,16,20,21,23,24]) The molecular field theory for magnetism demands that both θ and the cooperative transition temperature (T_{coop}) be linear combinations of the exchange parameters. Making the apparently reasonable assumption that two different exchange mechanisms could be operative in $CoSe_2$ and NiS_2, leads to two terms in the expressions for θ and T_{coop}. In a grossly simplified form these expressions may be written as $\theta = A + B$, $T_{coop} = A - B$, which according to the observed $T_{coop} = 0$ have the trivial solution $A = B = \theta/2$. In preference to this unlikely deduction we suggest that the molecular field description is in fact an inappropriate basis for the interpretation of these results, implying accordingly also an apparent failure of the Curie-Weiss law. (However, it should be noted that the proposed [7,24] itineracy of the unpaired e_g electrons may lead to an alternative interpretation of the anomalous θ-values. This possibility must unfortunately remain unexplored in view of the ambiguities attached to the suggested band schemes, *vide supra*.)

The present interesting examples of apparent break-down of the conventional molecular field theory of magnetism clearly merit further attention.

(iv) *Lack of cooperative magnetic phenomena.* The neutron diffraction data collected at 4°K (Table 2) definitely show no purely magnetic reflections for any of the compounds and the possible magnetic contributions to the nuclear reflections are very small. A good agreement between observed and calculated neutron jF^2-values was obtained at both 4°K and room temperature when only nuclear contributions were assumed. (The somewhat poorer agreement at 4°K can be attributed to the fact that the JEEP I reactor was used as neutron source in this case, whereas the room temperature data have benefited from the increased neutron flux of the JEEP II reactor.)

A small magnetic contribution to the nuclear peaks is hard to detect, but from the agreement between jF_o^2 and jF_c^2 shown in Table 2 the ordered moment must in any case be small, probably less than 0.1 B.M. In order to ascertain the absence of magnetic ordering we plan to reexamine these compounds using the polarization analysis technique.

The present result for $CoSe_2$ contradicts that by Adachi *et al.*[23] who report that this compound obtains an antiferromagnetically ordered structure of the $MnSe_2$ type below $T_N = 93$°K.

Acknowledgements. The authors are grateful to Dosent H. A. Øye, *Norges tekniske høgskole* for performing the differential thermal analyses. S.F. wishes to thank *Norges almenvitenskapelige forskningsråd* for financial support.

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Received January 20, 1969.