Compounds with the Marcasite Type Crystal Structure

VI.* Neutron Diffraction Studies of CrSb₂ and FeSb₂

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Powder samples of $CrSb_2$ and $FeSb_2$ have been subjected to neutron diffraction studies between 4.2 and 298°K. Both compounds are found to retain the marcasite type crystal structure throughout this temperature range. $FeSb_2$ shows no evidence of magnetic ordering at 4.2°K, whereas $CrSb_2$ undergoes a transition to an antiferromagnetic state at a Néel temperature of 273 ± 2°K. The antiferromagnetic structure of $CrSb_2$ is similar to that of $CrCl_2$ in that the magnetic unit cell requires a doubling of the b and c axes of the orthorhombic chemical cell. The moments are coupled ferromagnetically within (011) of the magnetic cell, those in adjacent planes being antiparallel. The unique magnetic axis in $CrSb_2$ is approximately perpendicular to (101), and the spin quantum number is 0.97(2) for Cr, corresponding to two unpaired electrons.

A s a continuation of previous work [1-5] on compounds crystallizing with the FeS_2-m (m = marcasite) type structure, neutron diffraction studies have been carried out on the members $CrSb_2$ and $FeSb_2$ of this class.

An inspection of published data [3,6-9] reveals an apparently anomalous temperature dependence in the paramagnetic susceptibility of both compounds. Adachi *et al.*[9] have recently published an interpretation of this in the case of $CrSb_2$, based on a model previously used to explain a similar χ-T relationship for FeSi.[10] This model involves a temperature dependent population of two distinct spin states for the chromium atoms, *viz.* a diamagnetic ground state with $S = 0$ (singlet) and a paramagnetic excited state with $S = 1$ (triplet) which are separated by an energy gap of 0.07 eV. A good agreement with the experimental χ-T curve was obtained with reasonable values for all variable

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parameters. An essential consequence of the model is a lack of cooperative magnetism in the compound.

We have found that there is in fact magnetic ordering below 0°C, thus invalidating the conclusions of Adachi et al.[9] It is remarkable that a cooperative transition temperature at the ice point has escaped the attention of these authors. This can be ascribed to the fact that their neutron diffraction and specific heat data covered the region above room temperature, whereas their low temperature electrical resistivity measurements were restricted to below 0°C.

A recent consideration [11] of the chemical bonding in compounds having the FeS_2-m type structure predicts a high-spin d^2 configuration for Cr in $CrSb_2$ and a low-spin d^4 configuration for Fe in $FeSb_2$. While the paramagnetism observed for $CrSb_2$ is broadly speaking compatible with this prediction, the paramagnetic behaviour of $FeSb_2$ clearly requires explanation.

A further interest in this problem arose from the fact that no unambiguous evidence has hitherto been found for magnetic ordering in compounds with the FeS_2-m type structure. This is in marked contrast with the wide variety of cooperative magnetic phenomena observed [12-16] for compounds with the closely related FeS_2-p (p = pyrite) type structure.

EXPERIMENTAL

The samples were prepared as described in a preceding paper [1] and their homogeneities were ascertained from Guinier photographic X-ray data. Only samples with the stoichiometric 1:2 composition were utilized in the present study.

Powder neutron diffraction data were collected at temperatures between 4.2 and 298°K, using cylindrical sample holders of aluminium or vanadium. Neutrons of wavelength 1.186 and 1.860 Å were obtained from the reactor 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 ($b_{Cr} = 0.352 \times 10^{-12}$ cm, $b_{Fe} = 0.95 \times 10^{-12}$ cm, and $b_{Sb} = 0.54 \times 10^{-12}$ cm) were taken from the table published by The Neutron Diffraction Commission.[17] The magnetic form factor for Cr^{2+} calculated by Watson and Freeman [18] was used. In the case of $CrSb_2$ the least squares profile refinement programme of Rietveld [19] was applied in the final fitting of the variable parameters to the observed intensity data.

Throughout this paper the calculated standard deviations are appended in brackets after the corresponding parameter values, only the last digit(s) being given in each case. (The observed and calculated intensity data are available from the authors upon request.)

RESULTS AND DISCUSSION

(i) *Antiferromagnetism in* $CrSb_2$. The neutron diffraction pattern of $CrSb_2$ obtained at room temperature showed only reflections due to the nuclear structure in agreement with the findings of Adachi et al.[9] The dimensions of the orthorhombic chemical unit cell are $a_C = 6.0275(6)$ Å, $b_C = 6.8738(9)$ Å, and $c_C = 3.2715(7)$ Å. In terms of space group $Pnnm$ the FeS_2-m type atomic arrangement places 2Cr in position (a) $0,0,0$; $\frac{1}{2},\frac{1}{2},\frac{1}{2}$ and 4Sb in position (g) $\pm(x,y,0$; $\frac{1}{2}+x,\frac{1}{2}-y,\frac{1}{2})$. Least squares refinements on the basis of the room temperature data gave $x = 0.1797(2)$ and $y = 0.3662(2)$ for the positional parameters, in excellent agreement with the values $x = 0.180(1)$ and $y = 0.367(1)$ found by

means of X-ray diffraction.[2] Since departures from the symmetry of the space group *Pnnm* have been observed for a number of isostructural compounds,[4,5] refinements in terms of the alternative space group *Pnn2* were also attempted, but these calculations produced no convergence. This failure was attributed to the small number of reflections with $l \neq 0$ which were accessible through the use of a powder sample. Although $CrSb_2$ may in fact possess the space group *Pnn2*, the excellent reliability factor $R = \sum |jF_o^2 - jF_c^2| / \sum jF_o^2 = 0.031$ obtained on the basis of *Pnnm* shows that the latter space group provides at least a very good approximation. Since the Sb atoms are non-magnetic, these two alternatives give moreover identical results for all magnetic structures.

Neutron diffraction patterns obtained at liquid helium and liquid nitrogen temperatures showed additional reflections which were clearly of magnetic origin. These reflections could be indexed on an orthorhombic unit cell of dimensions $a_M = a_C$, $b_M = 2b_C$, and $c_M = 2c_C$. A number of possible arrangements for the moments on the Cr sites were considered, of which the solution depicted in Fig. 1 gave the best agreement with the observations. The antifer-
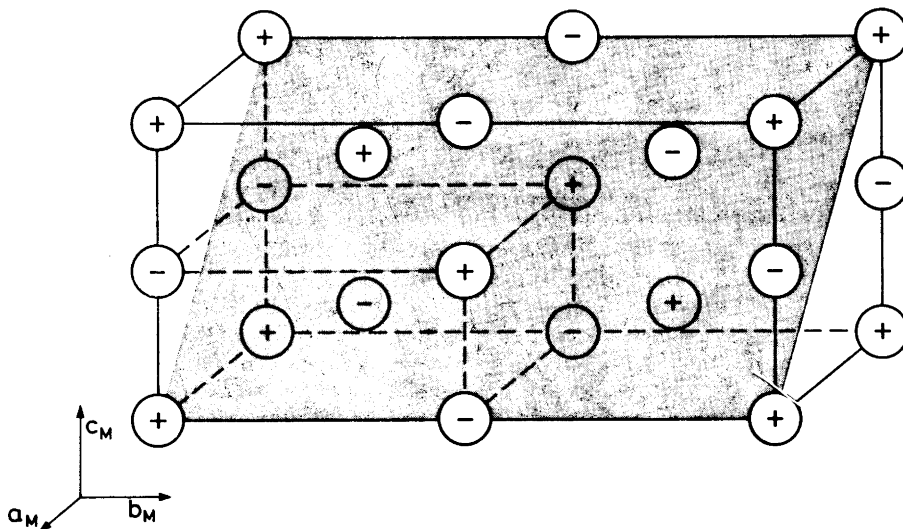

Fig. 1. The antiferromagnetic structure of $CrSb_2$. The magnetic and chemical unit cells represented by full and broken lines, respectively. The non-magnetic Sb atoms are omitted, for clarity. Only the phase relationships of the moments are shown, their directions being approximately perpendicular to the indicated diagonal plane (101) of the magnetic unit cell.

romagnetic structure of $CrSb_2$ is of the simple uniaxial type. The phase relationships of the moments are such that these are coupled ferromagnetically within (011) of the magnetic cell, the moments in adjacent planes being antiparallel.

The profile refinement procedure was applied to the neutron diffraction data obtained at 80°K, which had the best resolution. The following parameters were refined: the scale factor, the counter zero point, three profile parameters,

the unit cell dimensions, the positional parameters (x,y) of Sb, and the components $(2S_1, 2S_2, 2S_3)$ of the moment along the a, b, and c axes. The first least squares refinements showed that S_2 was only insignificantly different from zero, and this parameter was accordingly fixed at zero in the final calculations. A systematic deviation between the observed and calculated profiles for the low angle reflections during the first refinement cycles demonstrated the need for an asymmetry correction (*cf.* Rietveld [19]). A constant temperature factor of 0.20 $\mathring{A}^2$ was used for both kinds of atom.

The refinement process was continued until negligible shifts were obtained for all variables and was terminated at $R_{nucl.} = 0.048$, $R_{magn.} = 0.090$,* and $R_{profile} = 0.115$ for the reliability factors as defined by Rietveld.[19] (A similar refinement on the basis of the liquid helium data led to virtually identical values for all parameters, but gave somewhat larger standard deviations and reliability factors due to a poorer resolution.) Fig. 2 shows the fit obtained between the experimental points and the calculated peak profiles. Reflections with k and l even are purely nuclear, whereas those with k and l odd are purely magnetic. A further condition on the magnetic reflections is $2h + k + l = 4n + 2$. 77 reflections with $2\theta \leq 82°$ were included in the least squares refinement, omitting those in the intervals $44 - 48°$ and $53.5 - 55.5°$ due to overlapping Al-reflections from the cryostat.

The following values (with standard deviations) are obtained for the crystallographic and magnetic parameters at $80°K$: $a_C = 6.0183(4)$ $\mathring{A}$, $b_C = 6.8736(2)$ $\mathring{A}$, $c_C = 3.2704(2)$ $\mathring{A}$, $x_{Sb} = 0.1792(5)$, $y_{Sb} = 0.3643(4)$, $S_1 = 0.70(2)$, $S_2 = 0$ (fixed), and $S_3 = 0.67(3)$. The crystallographic changes which have occurred between 298 (*vide supra*) and $80°K$ can be attributed to thermal contraction and magnetostriction. The direction of the moments is, within the limits set by the experimental accuracy, perpendicular to the diagonal plane (101) of the magnetic unit cell (see Fig. 1). The size of the atomic moment corresponds to a spin quantum number $S_{Cr} = 0.97(2)$, which is in excellent agreement with the value expected for two unpaired electrons per Cr atom, when the orbital contributions are assumed to be negligible.

The temperature dependence of the integrated intensity of the magnetic (011) reflection is shown in Fig. 3, together with a scaled Brillouin function for $S = 1$. The systematic deviation between the two curves is of the same kind as, *e.g.*, found for EuTe,[20] and the discrepancy may be attributed to a small contribution from biquadratic terms [21] in the exchange interactions. The Néel temperature of $CrSb_2$ is according to Fig. 3 $T_N = 273 \pm 2°K$. No magnetic scattering other than the normal paramagnetic was observed above T_N, showing that the transformation at this temperature is a normal one, between an antiferromagnetic and a paramagnetic state.

No evidence of this transformation is to be found in the existing magnetic susceptibility curves for $CrSb_2$.[3,7,9] The electrical resistivity and heat capacity measurements of Adachi *et al.*[9] narrowly avoid the relevant temperature region. On the basis of the present results, the magnetic susceptibility curve(s) for $CrSb_2$ can in principle be accounted for in the intervals $T < T_N$ and $T > T_{max}$

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* The higher value of $R_{magn.}$ than of $R_{nucl.}$ can clearly be attributed to the relatively few resolved magnetic reflections, and their rapid decrease in intensity with increasing scattering angle.
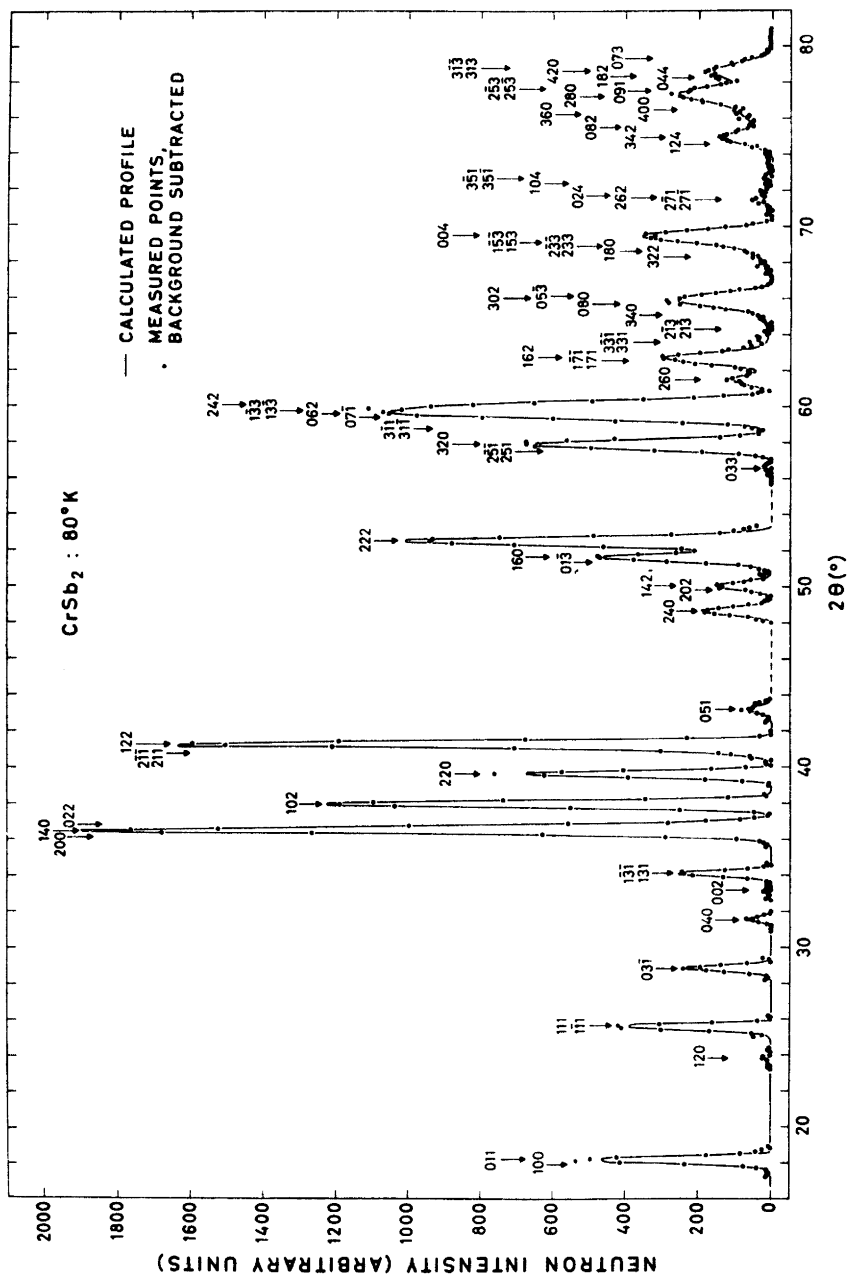
Fig. 2. Neutron powder diffraction diagram of $CrSb_2$ taken at 80°K ($\lambda = 1.860$ Å). The solid curve shows the calculated intensity profile, and the points are experimentally obtained by the step-scanning technique.

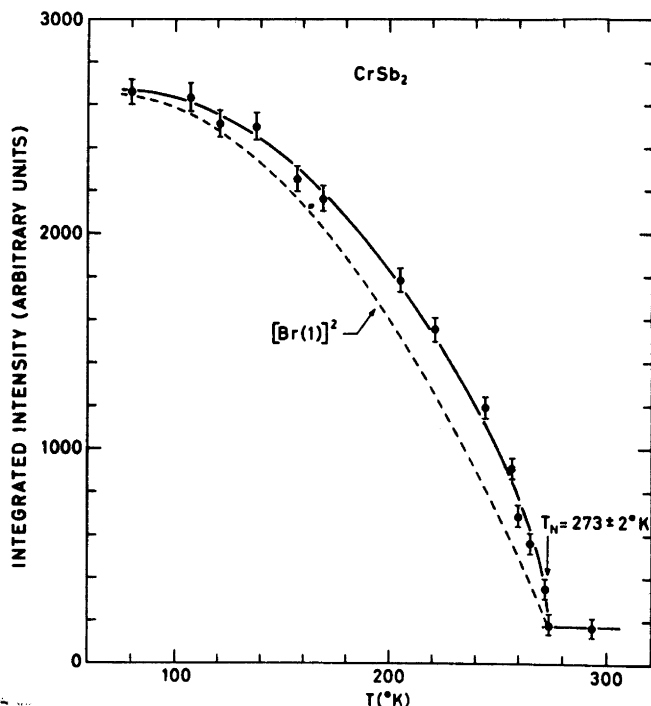*Fig. 3.* Temperature dependence of the integrated intensity of the magnetic (011) reflec-
tion for CrSb₂.

($T_{max} \approx 510°K$ corresponds to the maximum in $\chi(T)$). In order to explain the
(anomalous) behaviour of χ in the intermediate region $T_N < T < T_{max}$ a further
investigation of other physical properties is required.

A similar magnetic structure has been reported [22] for $CrCl_2$, which crystal-
lizes in space group *Pnnm* with a distorted TiO_2-r (r = rutile) type structure.
The crystal structures of $CrSb_2$ and $CrCl_2$ are closely related, the main difference
being that there occur pairs of non-metal atoms in the former, as compared
with single non-metal atoms in the latter structure. This distinction, together
with that between the non-metal components, results in different valence
states for Cr in the two compounds, which is reflected in their number of un-
paired electrons, *viz.* high-spin d^2 configuration ($S_{Cr} \approx 1$) in $CrSb_2$ and high-
spin d^4 configuration ($S_{Cr} \approx 2$) in $CrCl_2$. Another possible difference between the
magnetic structures of $CrSb_2$ and $CrCl_2$ concerns the orientation of the unique
magnetic axes. This has not been definitely established in the case of $CrCl_2$,
where the suggested direction of the moments is parallel to the longest Cr − Cl
bond, *i.e.* parallel to (001).

Bertaut [23] has applied his lattice theory of spin configuration to $CrCl_2$,
showing that a number of magnetic arrangements are potentially available for
the symmetry of the crystal structure. However, corresponding to the observed

connection between the chemical and magnetic unit cells, there is but one solution to the phase relationships of the moments. This is the solution shown in Fig. 1, and the theory is accordingly consistent with the experimental findings both for $CrCl_2$ and $CrSb_2$. In these considerations Bertaut employs four exchange parameters. J_1, J_2, and J_3 represent the interactions between nearest neighbour pairs of magnetic atoms along the a, b, and c axes, respectively, and J_4 is the corresponding parameter along the body diagonal. Corresponding to the physically real solution, Bertaut arrived at the following stability conditions:

$$J_1 > 0; \; J_2 < 0; \; J_3 < 0; \; J_2 \cdot J_3 > J_4^2$$

In the case of $CrSb_2$, it seems probable that J_3 has the greater numerical value of these parameters.

(ii) *Absence of cooperative magnetism in FeSb₂.* Neutron diffraction data for $FeSb_2$ collected at liquid helium and room temperatures show no purely magnetic reflections, and any contributions of magnetic origin to the nuclear reflections must be very small. Assuming only nuclear contributions, satisfactory agreement between jF_o^2 and jF_c^2 was obtained at both temperatures, R-values of 0.076 and 0.068 being obtained at 298 and 4.2°K, respectively. The least squares refinement of the nuclear structure on the basis of space group *Pnnm* gave $x = 0.1885(2)$ and $y = 0.3561(4)$ for the positional parameters at room temperature, in excellent agreement with the values obtained by X-ray diffraction techniques.[4] Attempts to refine the neutron diffraction data in terms of space group *Pnn2*, resulted in divergence, and one was therefore unable to verify the lack of the mirror plane perpendicular to (001). The absence of this has, however, previously been ascertained from three-dimensional single crystal X-ray data.[4] A small magnetic contribution to the nuclear peaks is difficult to detect, but we estimate that any possible ordered moment in $FeSb_2$ must be less than 0.1 B.M. The results exclude the possibility of a normal cooperative magnetic phenomenon occurring in $FeSb_2$, thus contradicting the suggestion made by Rosenqvist.[8]

In the light of the present findings, the magnetic susceptibility curve for $FeSb_2$ shows an anomalous temperature dependence which may be caused by the presence of discrete and/or dissolved impurities in the measured samples.[3,8] Further investigations on samples of improved purity seem to be required.

(iii) *Comparative data for FeAs₂ and NiSb₂.* Among the binary pnictides with FeS_2-*m* type structure, $FeAs_2$[3] is found to have virtually temperature independent paramagnetism, whereas $NiSb_2$[3] is diamagnetic. In order to make a comparison with the case of $FeSb_2$ (*vide supra*), neutron diffraction diagrams of these compounds were taken at room temperature.

The observed intensity data showed (as expected) no evidence of cooperative magnetism, and least squares refinements of the positional parameters in terms of space group *Pnnm* gave

$FeAs_2$: $x = 0.1636(9)$, $y = 0.3608(7)$; with $R = 0.075$
$NiSb_2$: $x = 0.2196(15)$, $y = 0.3601(6)$; with $R = 0.049$

in good agreement with the corresponding values established by means of X-ray diffraction.[2] The final reliability factors of these calculations are com-

parable with those obtained for $FeSb_2$, which give further support for the inferred negligible moment in that compound.

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