Compounds with the Marcasite Type Crystal Structure

VI.* Neutron Diffraction Studies of CrSb₂ and FeSb₂

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Powder samples of CrSb₂ and FeSb₂ 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. FeSb₂ shows no evidence of magnetic ordering at 4.2 K, whereas CrSb₂ undergoes a transition to an antiferromagnetic state at a Néel temperature of 273 ± 2 K. The antiferromagnetic structure of CrSb₂ is similar to that of CrCl₂ 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 CrSb₂ is approximately perpendicular to (101), and the spin quantum number is 0.97(2) for Cr, corresponding to two unpaired electrons.

As a continuation of previous work ¹⁻⁸ on compounds crystallizing with the FeS₂ₙ⁻m (m = marcasite) type structure, neutron diffraction studies have been carried out on the members CrSb₂ and FeSb₂ of this class.

An inspection of published data ³⁻⁹ 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 CrSb₂, 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

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. 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 of the chemical bonding in compounds having the FeS$_2$-m type structure predicts a high-spin $d^5$ 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 for compounds with the closely related FeS$_2$-p ($p$ = pyrite) type structure.

EXPERIMENTAL

The samples were prepared as described in a preceding paper 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°C, 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 $I_F$ by multiplication with $L^{-1}$. For the calculation of $F$-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. The magnetic form factor for Cr$^{3+}$ calculated by Watson and Freeman was used. In the case of CrSb$_2$ the least squares profile refinement programme of Rietveld 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. 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 $Pnma$ 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. Since departures from the symmetry of the space group \( Pnmm \) have been observed for a number of isostructural compounds, 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 \( \text{CrSb}_2 \) may in fact possess the space group \( Pnn2 \), the excellent reliability factor \( R = \frac{\sum|F_o| - |F_c|}{\sum|F_o|} = 0.03 \) obtained on the basis of \( Pnmm \) 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 antiferromagnetic structure of \( \text{CrSb}_2 \) 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,

\[ \text{Fig. 1. The antiferromagnetic structure of CrSb}_2. \text{ The magnetic and chemical unit cells represented by full and broken lines, respectively. The non-magnetic Sb atoms are omitted, for clarity. Only the phase relationships of the moments are shown, their directions being approximately perpendicular to the indicated diagonal plane (101) of the magnetic unit cell.} \]
the unit cell dimensions, the positional parameters \((x, y)\) of Sb, and the components \((2S_x, 2S_y, 2S_z)\) 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 Å\(^2\) was used for both kinds of atom.

The refinement process was continued until negligible shifts were obtained for all variables and was terminated at \(R_{\text{nucl}} = 0.048\), \(R_{\text{magn}} = 0.090\),* and \(R_{\text{profile}} = 0.115\) 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 \(2k + l = 4n + 2\). 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: \(a = 6.018(4)\) Å, \(b = 6.873(6)\) Å, \(c = 3.2704(2)\) Å, \(x_{\text{Sb}} = 0.1792(5)\), \(y_{\text{Sb}} = 0.3643(4)\), \(S_1 = 0.70(2)\), \(S_2 = 0\) (fixed), and \(S_3 = 0.67(3)\). The crystallographic changes which have occurred between 298 (\emph{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 \(S = 0.97(2)\), 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 \(T_N = 273 ± 2°K\). 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 \emph{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 \(T > T_{\text{max}}\).

* The higher value of \(R_{\text{magn}}\) than of \(R_{\text{nucl.}}\) 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 CrSb₂ taken at 80°K (λ = 1.860 Å). The solid curve shows the calculated intensity profile, and the points are experimentally obtained by the step-scanning technique.
(\(T_{\text{max}} \approx 510^\circ \text{K}\) corresponds to the maximum in \(\chi(T)\)). In order to explain the (anomalous) behaviour of \(\chi\) in the intermediate region \(T_N < T < T_{\text{max}}\) a further investigation of other physical properties is required.

A similar magnetic structure has been reported \(^{22}\) for CrCl\(_2\), which crystallizes in space group \(P\text{n}nm\) 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 unpaired electrons, viz. high-spin \(d^3\) configuration (\(S_{\text{Cr}} \approx 1\)) in CrSb\(_2\) and high-spin \(d^4\) configuration (\(S_{\text{Cr}} \approx 2\)) 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

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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 CrCl₂ and CrSb₂. 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 condi-
tions:

\[
J_1 > 0; \quad J_2 < 0; \quad J_3 < 0; \quad J_2 \cdot J_3 > J_4^2
\]

In the case of CrSb₂, 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
FeSb₂ 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, satisfac-
tory agreement between \( jF_{g}^2 \) and \( jF_{c}^2 \) was obtained at both temperatures,
\( R \)-values of 0.076 and 0.068 being obtained at 298 and 4.2°C, respectively. The
least squares refinement of the nuclear structure on the basis of space group
\( Pnbn \) 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. Attempts to refine the neutron diffraction data in
terms of space group \( Pn2n \), 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. A small magnetic contribution to the
nuclear peaks is difficult to detect, but we estimate that any possible ordered
moment in FeSb₂ must be less than 0.1 B.M. The results exclude the possibility
of a normal cooperative magnetic phenomenon occurring in FeSb₂, thus con-
tradicting the suggestion made by Rosenqvist.

In the light of the present findings, the magnetic susceptibility curve for
FeSb₂ shows an anomalous temperature dependence which may be caused by
the presence of discrete and/or dissolved impurities in the measured samples. Further investigations on samples of improved purity seem to be required.

(iii) Comparative data for FeAs₂ and NiSb₂. Among the binary pnictides
with FeS₂-m type structure, FeAs₂ is found to have virtually temperature
independent paramagnetism, whereas NiSb₂ is diamagnetic. In order to make
a comparison with the case of FeSb₂ (vide supra), neutron diffraction diagrams
of these compounds were taken at room temperature.

The observed intensity data showed (as expected) no evidence of co-
operative magnetism, and least squares refinements of the positional param-
eters in terms of space group \( Pnbn \) gave

\[
\begin{align*}
\text{FeAs}_2: \quad & x = 0.1636(9), \quad y = 0.3608(7); \quad \text{with } R = 0.075 \\
\text{NiSb}_2: \quad & x = 0.2196(15), \quad y = 0.3601(6); \quad \text{with } R = 0.049
\end{align*}
\]

in good agreement with the corresponding values established by means of
X-ray diffraction. 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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REFERENCES


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