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Preparation, Crystal Structure, and Magnetic Structure of $LiCrS_2$ and $LiVS_2$

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The crystal structures of $LiCrS_2$ and $LiVS_2$ are described. The anion–cation arrangement is like that in NiAs with ordering of Li and Cr (V) in alternating layers. The magnetic structure of $LiCrS_2$ which shows a spin ordering at 4.2°K was determined by means of neutron powder diffraction. The spin structure consists of a triangular arrangement within the hexagonal planes with antiparallel coupling between adjacent planes, i.e., an ordering of the third kind. In $LiVS_2$ no ordering was observed at 4.2°K.

Introduction

The crystal structures of $NaCrS_2$, $CuCrS_2$ and $AgCrS_2$ have been reported by Bongers *et al.* (*1*). These structures are based on a distorted cubic close packing of the S^{2-} ions with Cr^{3+} ions in the octahedral holes. In this way CrS_2^- sandwiches are formed, between which the monovalent cations are located (Na^+ in octahedral holes, Cu^+, and Ag^+ in tetrahedral holes). All structures are rhombohedral. The magnetic structures of these compounds are all rather complex (*2*).

The compound $LiCrS_2$ has been mentioned by Sergent and Prigent (*3*) who report it to have a cubic structure with $a = 6.04$ Å. This would mean that probably the structure is not related to that of the Na, Ag, and Cu compounds. This could of course been caused by the small ionic radius of Li^+, but it seemed to be of interest to investigate this compound more closely and to determine the crystallographic and the magnetic structure by means of X-ray and neutron powder diffraction.

As the isostructural compound $LiVS_2$ was also available its structural parameters were simultaneously determined.

Experimental

The sample of $LiCrS_2$ was prepared from Li_2CO_3 and Cr_2O_3 by mixing thoroughly and heating the mixture in a carbon crucible in a H_2S atmosphere at 500°C for 10 hr. The resulting product was powdered and heated in a H_2S atmosphere at 700°C for 24 hr and subsequently slowly cooled down. In the same way $LiVS_2$ was prepared from Li_2CO_3 and V_2O_3.

X-ray powder diagrams were taken with a Philips diffractometer (Cu K_α radiation) at room temperature. Neutron diffraction data have been collected on the powder diffractometer at the H.F.R. in Petten. The neutron wavelength was 2.5796 (4) Å, obtained from the (111) planes of a copper crystal. As a second-order filter a block of pyrolytic graphite with a thickness of 10 cm was employed (*4*). Between reactor and monochromator and in front of the BF_3 counter Soller slits with a horizontal angular divergence of 30′ were placed. The samples were contained in cylindrical vanadium sample holders with a diameter of 20 mm.

From both compounds neutron diffraction diagrams were taken both at room temperature and at liquid helium temperature. As absorption was small but not negligible (in both cases $\mu R = 0.57$) the data were corrected for this effect.

The magnetic susceptibility measurements were carried out with an automatic Faraday system constructed by Arbouw and Roelofsen (*5*) and with a parallel field vibrating sample magnetometer.

$LiCrS_2$ showed a Curie–Weiss behavior with values for the paramagnetic moment $\mu_{eff} = \sqrt{8\,C_{mole}}$ of 3.83 μ_B.

This value corresponds to a number of unpaired electrons μ of 2.96. The paramagnetic Curie temperature θ was −276°K. The susceptibility was slightly field dependent below 200°K. At low temperatures $LiCrS_2$ became antiferromagnetic with $T_N \approx 55$°K.

Crystal Structures

The X-ray diagrams of the two compounds showed the same intensity distribution and could both be indexed on the basis of a hexagonal cell with c/a ratios of 1.743 for $LiCrS_2$ and 1.816 for $LiVS_2$. Probably Sergent and Privent were mislead by the fact that in $LiCrS_2$ this ratio is close to $\sqrt{3}$ which makes it possible to assign cubic indices to the first part of the diagram. One unit cell contains only one formula unit.

Inspection of the X-ray intensities revealed that the sulphur atoms are arranged in hexagonally stacked layers with Cr or V in octahedral holes. For the position of the Li atoms there are a priori two possibilities:

(i) Li in octahedral holes. The structure can then be described as follows:

Space group: $P\bar{3}$ (C_{3i}^1), $P321$ ($D_3{}^2$), or $P\bar{3}ml$ (D_{3d}^3);
1 Cr (V) in (1a): 0,0,0;
1 Li in (1b): $0,0,\frac{1}{2}$;
2 S in (2d): $\pm(\frac{1}{3},\frac{2}{3},z)$ with $z \approx \frac{1}{4}$.

(ii) Li in tetrahedral holes. This results in the structure:

Space group: $P3$ ($C_3{}^1$) or $P3ml$ (C_{3v}^1)
1 Cr (V) in (1a): $0,0,z$ with $z \approx 0$;
1 Li in (1b): $\frac{1}{3},\frac{2}{3},z$ with $z \approx \frac{5}{8}$;
1S in (1b): $\frac{1}{3}$, $\frac{2}{3}$, z with $z \approx \frac{1}{4}$;
1 S in (1c): $\frac{2}{3}$, $\frac{1}{3}$, z with $z \approx \frac{3}{4}$.

In the structure refinements based on the neutron diffraction data both models have been refined by means of the profile method (*6*). This method determines the estimates of the various parameters by finding a least-squares fit between the observed and calculated profile intensities, minimizing the quantity

$$\chi_\nu{}^2 = \sum_i w_i[y_i(\text{obsd}) - y_i(\text{calcd})]^2/\nu,$$

where y_i(obsd) and y_i(calcd) are the observed and calculated values of the i-th measuring point, and w_i is its statistical weight. The number of points minus the number of parameters is indicated by ν. The coherent scattering lengths used are: $b_{Li} = -0.194 \times 10^{-12}$ cm, $b_{Cr} = +0.352 \times 10^{-12}$ cm, $b_V = -0.051 \times 10^{-12}$ cm, and $b_S = +0.28 \times 10^{-12}$ cm. In the case of $LiCrS_2$ the $\chi_\nu{}^2$ values after convergence were 6.0 and 10.3 for model (i) and model (ii), respectively, which means that the model with Li in octahedral holes fits the data significantly better than the other one. In $LiVS_2$ this effect is much more pronounced because the diffraction pattern is entirely due to the Li–S arrangement, the vanadium coherent scattering length being negligible. Model (i) leads to a $\chi_\nu{}^2$ value of 2.0, model (ii) to a value of 43.2. The observed diffraction profile of $LiVS_2$ together with the profiles calculated for the two different models (i) and (ii) is given in Fig. 1.

The above given results show unambiguously that in $LiCrS_2$ and in $LiVS_2$ both the Cr(V) atoms and the Li atoms are located in the octahedral holes of the hexagonal close-packed array of sulphur atoms. The final least-squares parameters are listed in Table I. The observed and calculated diffraction profiles of $LiCrS_2$ are shown in Fig. 2. The agreement is very satisfactory apart from the (004) reflection at 117° 2θ which is observed about twice as strong as calculated. The same discrepancy appeared in the 4.2°K diagram. It is not known whether this is due to an impurity or to a significant detail in the crystal structure. The intensity calculated for this reflection on the basis of model (ii) is only about 7% higher than on the basis of model (i). The most important interatomic distances in both compounds are given in Table II.

Magnetic Ordering at 4.2°K

The neutron diagram at 4.2°K of $LiVS_2$ did not show any magnetic ordering.

In the case of $LiCrS_2$ the low-temperature diagram showed clear magnetic peaks, all of which occurred in directions other than the nuclear scattering, indicating that no ferromagnetic component is present in the spin arrangement. The magnetic peaks could all be indexed on a hexagonal cell with dimensions $a = a_0\sqrt{3}$ and $c = 2c_0$ where a_0 and c_0 are the dimensions of the crystallographic cell. The observed reflection conditions are $h - k = 3n$, $l = 2n$ for the nuclear intensities and $h - k \neq 3n$, $l = 2n + 1$ for the magnetic intensities. An alternative description of the periodicity of the magnetic lattice is that based on the crystallographic cell with a propagation vector in reciprocal space: $\mathbf{k} = 1/3, 1/3, 1/2$.

From the reflection condition $l = 2n + 1$ it follows immediately that each Cr moment has

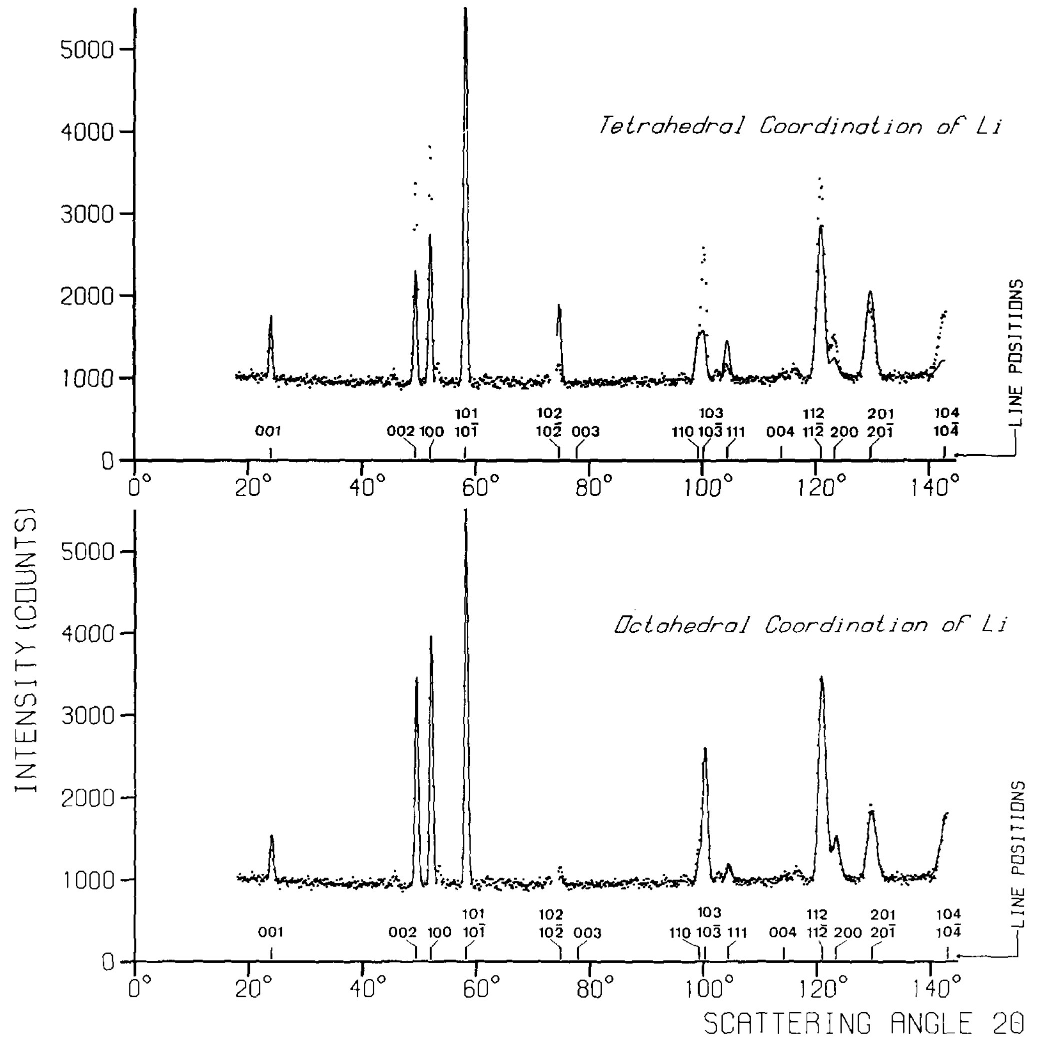

FIG. 1. Neutron diffraction profiles of $LiVS_2$ at room temperature. The observed profile is represented by dots. The full line in the upper diagram is the profile based on the model with tetrahedral coordination of Li, that in the lower diagram is based on a model with octahedral coordination of Li.

TABLE I

MAGNETIC AND STRUCTURAL PARAMETERS IN $LiCrS_2$ AND $LiVS_2$[a]

	$LiVS_2$	$LiCrS_2$	
Temp (°K)	293	293	4.2
a (Å)	3.3803(2)	3.4637(3)	3.4515(3)
c (Å)	6.1381(5)	6.0369(11)	6.0212(10)
c/a	1.8158(4)	1.7429(6)	1.7445(6)
z (S)	0.235 (1)	0.220 (2)	0.224 (1)
μ_{Cr} (μ_B)	—	—	2.26 (6)
$\chi_v{}^2$	2.0	6.0	5.0

[a] Standard deviations, based on statistics only, in units of the last decimal place are given in parentheses.

antiparallel partners at $\pm c_0$. The condition $h - k \neq 3n$ indicates that the vector sum of the moments in each magnetic cell equals zero. From a closer inspection of the diagram it was deduced that all moments are in the hexagonal basal plane.

Thus the spin structure can be described as a triangular arrangement within the hexagonal planes with antiparallel coupling to the moments in adjacent planes (Fig. 3). The magnetic scattering cross section of reflections (hkl) with $(h - k) \neq 3n$ is for this type of structure:

$$\sigma_{hkl} = 0.2695^2 \mu_{Cr}^2 f_{Cr}^2 [9/4 - 3d_{hkl}^2 a^{*2}(h^2 + hk + k^2)],$$

where μ_{Cr} is the Cr moment, f_{Cr} its form factor and d_{hkl} the interlattice spacing.

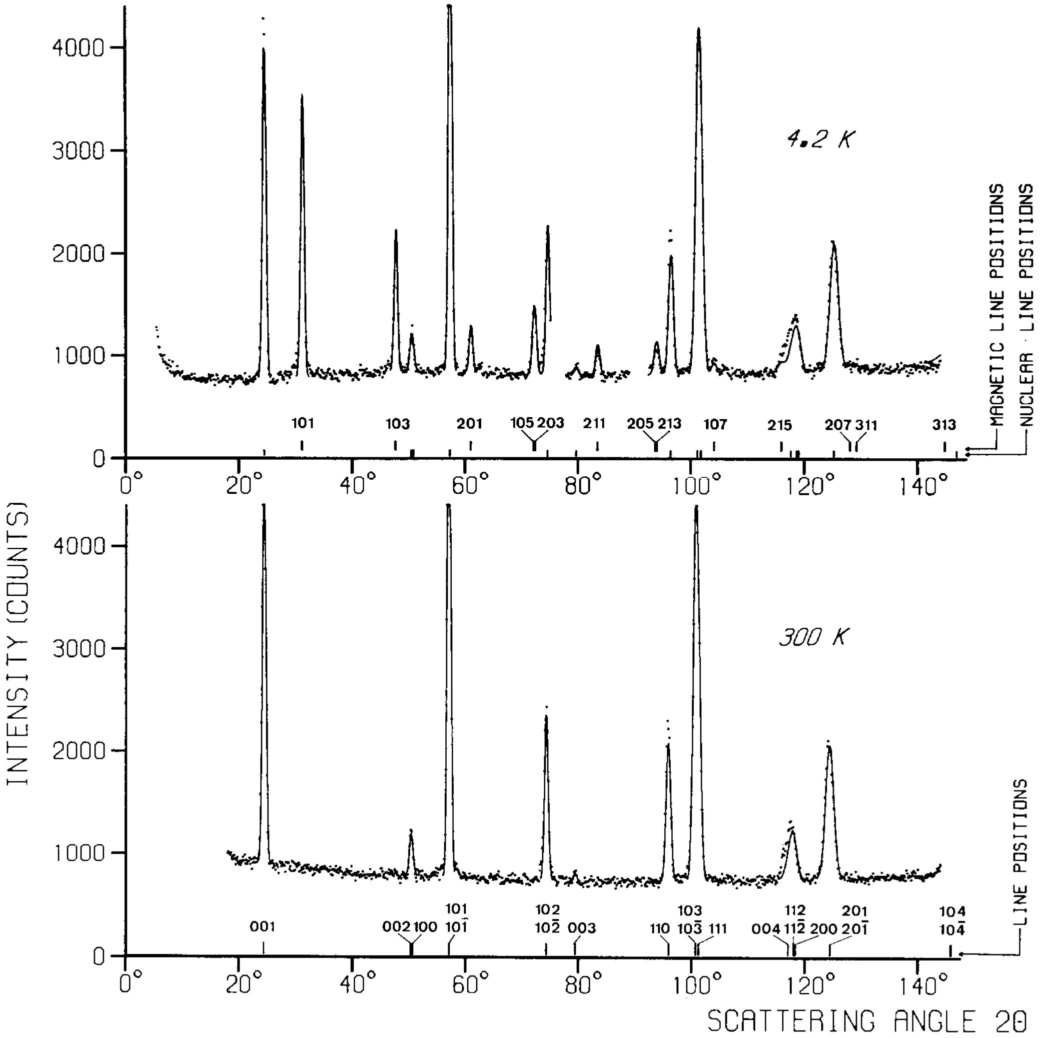

FIG. 2. Observed and calculated neutron diffraction profiles of LiCrS$_2$ at two different temperatures. The dots represent the observed profile, the full line the calculated profile. In the diagram at 4.2°K the angular regions where copper lines of the cryostat occur (at 76° and 91° 2θ) have been omitted. The Miller indices of the nuclear reflections refer to the crystallographic unit cell, those of the magnetic reflections to the magnetic unit cell.

A particular feature of this structure is that its scattering cross section only depends on the magnitude of the Cr moment and not on the absolute orientation of the triangular pattern in the hexagonal plane as long as the relative orientation with 120° angles is conserved. This means that diffraction methods (also single crystal) are unable to retrieve the absolute spin directions. Furthermore the magnetic intensity is equal for all members of a form $\{hkl\}$; all crystallographically equivalent reflections are also magnetically equivalent.

The final structural and magnetic parameters at 4.2°K, obtained with line profile refinement, are listed in Table I. In the refinement the spherical form factor for Cr^{3+} of Watson and Freeman (7) was used. The observed and calculated profiles are shown in Fig. 2.

Discussion

In NaCrS$_2$, AgCrS$_2$, and CuCrS$_2$ adjacent chromium layers are shifted over 2/3, 1/3, 1/3 with respect to each other, resulting in a rhombohedral structure. In the present compounds the Cr(V) layers are not shifted along the *a* and *b* axes.

As the Li layers in between are arranged likewise,

TABLE II

INTERATOMIC DISTANCES IN $LiCrS_2$ AND $LiVS_2$ AT ROOM TEMPERATURE[a]

	$LiVS_2$	$LiCrS_2$
Li-6Li	3.3803(2)	3.4637(3)
Cr(V)-6Cr(V)	3.3803(2)	3.4637(3)
Li-2Cr(V)	3.0691(3)	3.0184(6)
Li-6S	2.54(1)	2.62(1)
Cr(V)-6S	2.43(1)	2.40(1)
S-6S	3.3803(2)	3.4637(3)
S-3S	3.48(1)	3.32(2)
S-3S	3.80(1)	3.93(2)

[a] Standard deviations in units of the last decimal place are given in parentheses.

a trigonal unit cell is obtained with a *c* axis that is about one-third of that of the rhombohedral compounds. Both Li and Cr(V) are located in octahedral interstices between sulphur layers. As far as the authors are aware the present compounds are the first sulphur compounds in which Li is six coordinated. The Cr–S distances in $LiCrS_2$ are comparable with the distance observed in other compounds, while the Li–S distances are a few percent larger than in Li_2S, where Li is four coordinated, which is quite acceptable.

An interesting feature of the present structures is that disordering of Li and Cr(V) would lead to a structure of the NiAs type. This is the first known example of such an "ordered" NiAs type structure.

As regards the magnetic structure it may be noted that the symmetry elements in D_{6h} which leave the observed propagation vector $\mathbf{k} = (1/3, 1/3, 1/2)$ invariant are the same as those contained in space group $P321$. Thus these symmetry elements constitute the group of **k** if the structure belongs to one of the space groups $P321$ or $P\bar{3}ml$. If the crystallographic space group is $P\bar{3}$ the group of **k** contains only the identity element and the 120 and 240° rotational elements. In this case $(1/3, 1/3, 1/2)$ is a point in the Brillouin zone with the same symmetry as that of the more general vector $(1/3, 1/3, \mu)$ which means that in this space group the observed doubling of the c axis is purely accidental. Therefore, it is most probably that the space group of $LiCrS_2$ is $P321$ or $P\bar{3}ml$.

As all groups of **k** mentioned above contain the trigonal axis as symmetry element not only the crystallographic but also the magnetic structure is trigonal.

The present structure type, an antiferromagnetic ordering of the third kind, has not been observed very frequently. Other examples are CrSe, reported by Corliss *et al.* (*8*) and $RbNiCl_3$ and $CsNiCl_3$, reported by Minkiewicz, Cox, and Shirane (*9*). In the latter compounds the magnetic unit cell is the same as in $LiCrS_2$ but the spins rotate in a plane perpendicular to the basal plane instead of in this plane.

The observed moment of Cr^{3+} is considerably smaller than the expected value of 3 μ_B. The difference is presumably due to covalency effects which can considerably alter the distribution of the magnetic moments around the Cr^{3+} ion.

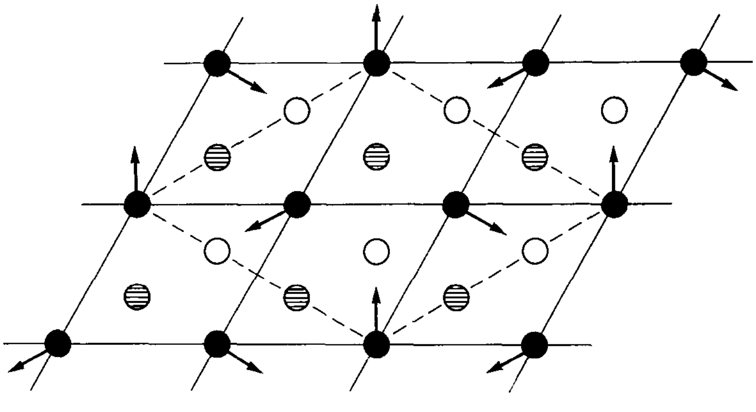

FIG. 3. Spin arrangement in $LiCrS_2$ within one hexagonal chromium layer. In adjacent layers the moments are reversed. The chemical cell is shown in dark outline, the magnetic cell is indicated by the dashed lines. The black circles represent the chromium atoms, the open and shaded circles represent sulphur atoms at $z \approx \frac{3}{4}$ and $z \approx \frac{1}{4}$, respectively.

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