

Crystallography at 0.3 Å: Single-Crystal Study of $\text{Cr}(\text{NH}_3)_6\text{Cr}(\text{CN})_6$ at the Cornell High-Energy Synchrotron Source

BY FINN S. NIELSEN, PETER LEE AND PHILIP COPPENS*

Chemistry Department, State University of New York at Buffalo, Buffalo, NY 14214 and CHESS, Cornell University, Ithaca, NY 14853, USA

(Received 3 September 1985; accepted 2 January 1986)

Abstract

Short-wavelength ($\lambda = 0.302 \text{ \AA}$) synchrotron radiation at CHESS has been used to analyze the crystal and electronic structure of hexaamminechromium(III) hexacyanochromate(III), $\text{Cr}(\text{NH}_3)_6\text{Cr}(\text{CN})_6$, using a total of 7224 intensity measurements. Special attention is given to corrections for counter deadtime, beam-polarization effects and second-order contamination of the beam. An unequal step-size method is introduced to improve sampling of the extremely narrow diffraction peaks. Structural and experimental data are: $R\bar{3}$, $a = b = c = 7.4635 (7) \text{ \AA}$, $\alpha = \beta = \gamma = 97.830 (10)^\circ$, $V = 419.3 \text{ \AA}^3$, $Z = 1$, $R = 0.0285$ for 1968 independent reflections and 44 parameters. Deformation density maps show bond and lone-pair features and contain remarkably little noise in regions away from the atoms. The study shows that excellent quality data can be obtained with synchrotron radiation, in particular when small crystal size is combined with short wavelengths.

Introduction

Though synchrotron radiation has been available for several years there are as yet no fully three-dimensional crystal studies of the accuracy commonly achieved in small-molecule structure analysis with conventional sources. This is in part due to the scarcity of synchrotron beamtime and less than ideal beam stability. Nevertheless, synchrotron radiation, if stable, has significant advantages. It is intense, thus permitting the use of small crystals, it has a very small divergence and it can be tuned to very short wavelengths, in particular when the experiment is performed at a wiggler beamline.

The accessibility of short wavelengths is in particular useful when high-order intensities are enhanced by reduction in data-collection temperature. But before such an experiment can be performed it is necessary to assess the beam stability, both in intensity and in space, and its effect on the accuracy of the diffracted intensities. We report here

such a feasibility study, performed at the A2 beamline at CHESS, the Cornell High Intensity Synchrotron Source, where a single-crystal diffraction station has been constructed (Nielsen, Coppens & Batterman, 1984).

In order to be able to judge the precision of the measurements a highly symmetric crystal with moderately sized unit cell was selected. Crystals of $\text{Cr}(\text{NH}_3)_6\text{Cr}(\text{CN})_6$ are isomorphous with $\text{Co}(\text{NH}_3)_6\text{Co}(\text{CN})_6$ and $\text{Co}(\text{NH}_3)_6\text{Cr}(\text{CN})_6$ studied by Iwata & Saito (1973) and Iwata (1977) respectively. They are rhombohedral and belong to the space group $R\bar{3}c$. They are relatively hard and thus permit the collection of data to larger values of $\sin \theta/\lambda$. This work forms part of a combined X-ray/polarized-neutron study of the charge and spin density in the paramagnetic crystals.

Instrumentation

The six-pole wiggler which is inserted in the CHESS A2 beamline produces high-energy radiation with a critical wavelength of 0.55 \AA at the current field strength of 1.4 T. The radiation is monochromatized with a double-silicon-crystal monochromator, a first version of which was described by Tischler (1983). The first crystal is water-cooled, while the second crystal can be fine-tuned with a piezoelectric crystal to compensate for variation of the heat load on the monochromator as the synchrotron electron beam decays. The fine-tuning is achieved with a feedback loop which maximizes the intensity in a monitor counter mounted on the incident-beam side of the diffractometer.

The Huber 512 diffractometer is mounted on a table with four adjustable jacks which allows translation along a horizontal axis perpendicular to the beamline, rotation around such an axis and around a horizontal axis parallel to the beam, as well as adjustment of the vertical height.

The diffractometer is controlled by a PDP11/23 computer with a software package, *HUBER*, developed specifically for synchrotron radiation. It was originally based on the program *SYNDAS* by Kwick, McMullan & Koetzle (1983). Features of the

* Author to whom correspondence should be addressed.

package include autoindexing, reflection search and centering, and unequal step-width scan capability. The piezo crystal is controlled semi-continuously through a concurrently running background program.

Experimental

A crystal of about 0.1 mm size was grown by slow diffusion of solutions of 0.25 g [Cr(NH₃)₆]Cl₃ and 0.25 g Na₃[Cr(CN)₆] each in 5 ml distilled water each through a silica gel. When the apparatus was placed in a refrigerator, crystals grew in 10–15 d (Tanaka, 1984).

A wavelength of 0.302 Å was selected for the experiment. The combination of hard radiation with small crystal size effectively eliminates extinction and absorption effects in the sample. As the reflections are extremely narrow (FWHM is typically 0.010°) reflections initially were located by Polaroid photography rather than by search techniques. An orientation matrix and cell dimensions were obtained from the diffractometer setting angles of 25 reflections. A total of 7224 reflections with $(\sin \theta)/\lambda < 1.15 \text{ \AA}^{-1}$ were collected in a 9 d period, using a scan width of 0.5° and a non-isometric (ω) step scan with steps which varied between 0.005° at the center and 0.02° in the tails of the reflection, as described more fully in the Appendix. This non-equal step is necessitated by the extreme sharpness of the central peak and the long tails of the reflection profile.

Data were processed with a program specifically modified for synchrotron measurements. It allows for the unequal step width in the scans, for a polarization factor appropriate for a partially polarized beam, and for a correction for a non-continuous source. Several of these features, as well as the effect of second-order contamination, are discussed briefly below.

Polarization correction

Since the degree of polarization was initially not known, and may be variable with instrumental alignment, the fraction c of vertical polarization is given as an input parameter and applied in the expression

$$\text{Pol. Fac.} = [c + (1 - c) \cos^2 2\theta] / 2.$$

Initially the data were processed and refined with several values of c . At a later stage of the experiment c was estimated from the ratio of the Compton scattering of a 0.125" (3 mm) block of aluminium measured in and perpendicular to the horizontal plane at an angle of 90° to the incident beam. With an incident-beam aperture of 0.5 × 0.5 mm and 41 keV photons a value of 0.885 ± 0.010 was derived in repeated measurements.

Deadtime corrections

For a non-continuous source with a pulse separation larger than the counter deadtime the relation between the corrected and the recorded number of counts is given by

$$N_{\text{corrected}} = -B \ln(1 - N_{\text{recorded}}/B), \quad (1)$$

where B is the number of bunches per second. This expression can be derived in a straightforward way from equations given by Arndt (1978) and Batterman (1978).

The orbital period of the electrons in the Cornell synchrotron is 2.56 μs. Since the machine was run in the three-bunch mode the average separation of the pulses is 0.85 μs. A first value of counter deadtime was estimated from an oscilloscope tracing of the counter output to be 0.7 μs. The correction obtained with expression (1) was checked by measuring 18 of the strongest reflections with a 0.5" (12 mm) aluminium attenuator positioned in the beam. Two sets collected with the attenuator before and after the monitor counter were in excellent agreement, after suitable correction for the attenuator factor, as may be expected for a highly monochromatic beam. But comparison of the attenuated measurements with those corrected according to (1) showed large discrepancies up to 40% for the reflections with the highest count rates. A modified formula based on expression (6) of Arndt (1978) was therefore used. It is valid for a deadtime after each recorded event bracketed by

$$n/B < \tau < (n+1)/B$$

and is given by

$$N_{\text{corrected}} = -B \ln \left(1 - \frac{N_{\text{recorded}}}{B - nN_{\text{recorded}}} \right). \quad (2)$$

A better agreement with the attenuated reflections was obtained with $n = 1$. However, reflections with large count rates were still considerably undercorrected. Part of the remaining discrepancy can be eliminated by applying a correction appropriate for a counter, rather than electronics-dominated deadtime (Arndt, 1978). But a baseline shift in the pulse-height analyzer occurring at very high count rates is believed to be the main cause of the remaining discrepancy. Selection of $n = 2$ in expression (2) led to a serious overcorrection of the moderately strong reflections. The counter deadtime is clearly bracketed between 0.85 and 1.7 μs. All measurements were therefore corrected with an n value equal to one, while values measured with an attenuator were used for the reflections with very high count rates.

Second-order contamination

The single-crystal monochromator will pass $\lambda/2$ radiation if the reflection with half the d -spacing of

the main reflection has a non-zero structure factor. Since a (400) plane of silicon was used in the experiment a correction for such second-order contamination may be necessary. To a large extent the higher-energy photons can be discriminated against by the pulse-height analyzer. A check was performed by measuring a number of reflections with half-integer Miller indices corresponding to half the reciprocal-lattice vector of strong reflections in the data set. The ratio of the F^2 values was found to be 0.06%, which corresponds to a contamination of about 0.2–0.3% if the λ^3 dependence of the integrated scattering and the difference in Lorentz factor are taken into account. For four weak reflections which occurred at half the reciprocal-lattice vector of a strong reflection, corrections up to 10% in F^2 were necessary. In all cases this correction improved the agreement between observed and calculated structure factors.

Integrated intensities were obtained with the program *PROFILE* (Blessing, Coppens & Becker, 1974). For the determination of the peak/background boundary the scan was assumed to consist of equidistant points.

Symmetry-related reflections were averaged to give 2329 unique data. Internal agreement factors, listed in Table 1, are comparable with or better than those of good quality conventional data sets.

Data refinement

The data were refined both with the Nonius *SDP* package and with the program *LINEX77* (Becker & Coppens, 1975). Since the two sets of results were essentially identical only the latter are discussed here.

Initial parameters were taken from the cobalt-cobalt complex studied also at room temperature by Iwata & Saito (1973). A total of 44 parameters were varied. Refinement of the 1968 independent reflections processed with $c=0.90$ proceeded rapidly to $R(F)=2.85\%$ and a goodness of fit of 1.77. Final values of Δ/σ were all less than 0.1.

Additional refinements with $c=0.95$ and $c=0.85$ gave identical agreement factors, but the temperature factors were systematically higher by about 1% for the lower degree of polarization. The remarkable lack of sensitivity to the degree of polarization is due to the limited range of θ values in this short-wavelength data set.

Subsequently a high-order refinement was carried out as a preliminary step for the calculation of X - X difference density maps. Since the two Cr atoms are located at (0, 0, 0) and $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ the dominant spherical component of the chromium charge density contributes only to reflections with $h+k+l$ even. The weak reflections with odd parity of the index sum are not observable at high Bragg angles in the room-temperature experiment and were only collected for $\sin \theta/\lambda$ values $<0.85 \text{ \AA}^{-1}$. In order to include a sig-

Table 1. *Crystallographic data*

Space group	$R\bar{3}$	
Cell constants	7.4635 (7) \AA^*	
$a = b = c$	97.830 (10) ^{o*}	
$\alpha = \beta = \gamma$	1	
Z	419.3 \AA^3	
V	0.302 \AA	
λ	186	
$F(000)$	362.28	
M_r	1.15 \AA^{-1}	
$(\sin \theta/\lambda)_{\text{max}}$		
Data processing		
No. of reflections collected	7225	
No. of reflections with $I > 3\sigma(I)$	5599	
No. of unique reflections	2329	
h, k, l limits	0 < h < 16; 0 < k < 16; -16 < l < 16	
Agreement factor, R_{int}	On intensity	On F_{obs}
with $n=1$ deadtime correction (see text)		
all reflections	0.021	0.030
observed reflections	0.020	0.016
observed and accepted reflections		
[236 reflections with deviations $>5\sigma(I)$ rejected]	0.012	0.015
Least-squares-refinement results		
All data		
No. of reflections [$>3\sigma(F)$]	1968	
No. of variables	44	
$R(F)$	0.0285	
$wR(F)$ [$w=1/\sigma^2(F)$]	0.0315	
S	1.77	
High-order data ($\sin \theta/\lambda > 0.7 \text{ \AA}^{-1}$)		
No. of reflections [$3 > \sigma(F)$]	1295	
No. of variables	31	
$R(F)$	0.0252	
$wR(F)$ [$w=1/\sigma^2(F)$]	0.0196	
S	0.83	

* Error excludes wavelength uncertainty estimated at $\Delta\lambda/\lambda = 2 \times 10^{-4}$.

nificant number of these weak reflections the high-order cut-off was chosen at a relatively low value of 0.7 \AA^{-1} . The refinement with 1295 reflections and 31 (non-hydrogen) parameters proceeded to a final $R(F)$ value of 2.52% and a goodness of fit of 0.83, indicating an improvement of the model relative to the full-data refinement. Final agreement factors and parameters are listed in Tables 1 and 2 respectively.*

Deformation density maps

X - X deformation density maps are given in Fig. 1. They show lone-pair peaks at the C and N atoms, bonding density in the CN bond and asymmetric features around the Cr atoms, with the negative areas being more shallow in directions away from the ligands. The map before averaging through the two CN groups (Fig. 1a) contains two different cuts through the crystallographically equivalent CN

* Lists of hkl , F_o , F_c and $\sigma(F_o)$ have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42738 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Positional and thermal parameters* (Å²)(a) Full refinement. (b) Refinement with $\sin \theta/\lambda > 0.7 \text{ \AA}^{-1}$.The temperature-factor expression is $T = \exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + U_{12}hka^*b^* + U_{13}hla^*c^* + U_{23}klb^*c^*)]$.

	x	y	z	U(1, 1)	U(2, 2)	U(3, 3)	U(1, 2)	U(1, 3)	U(2, 3)
Cr(1)(a)	0.0	0.0	0.0	0.02049 (6)	0.02049	0.02049	0.00282 (7)	0.00282	0.00282
(b)	0.0	0.0	0.0	0.02071 (9)	0.02071	0.02071	0.00277 (11)	0.00277	0.00277
Cr(2)(a)	0.5	0.5	0.5	0.01899	0.01899 (6)	0.01899	0.00305 (6)	0.00305	0.00305
(b)	0.5	0.5	0.5	0.01891 (8)	0.01891	0.01891	0.00307 (10)	0.00307	0.00307
C(1) (a)	0.2462 (1)	0.1323 (1)	-0.0513 (1)	0.0290 (4)	0.0309 (4)	0.0247 (3)	0.0011 (3)	0.0034 (3)	0.0048 (3)
(b)	0.2458 (3)	0.1313 (3)	-0.0509 (3)	0.0278 (4)	0.0318 (5)	0.0291 (4)	0.0002 (3)	0.0050 (3)	0.0067 (3)
N(1) (a)	0.3808 (1)	0.2107 (1)	-0.0753 (1)	0.0363 (4)	0.0600 (5)	0.0448 (4)	-0.0065 (4)	0.0077 (3)	0.0204 (4)
(b)	0.3821 (2)	0.2131 (2)	-0.0736 (2)	0.0350 (3)	0.0609 (6)	0.0467 (4)	-0.0099 (4)	0.0084 (3)	0.0208 (4)
N(2) (a)	0.5544 (1)	0.2578 (1)	0.3587 (1)	0.0323 (4)	0.0246 (3)	0.0292 (3)	0.0083 (3)	0.0049 (3)	0.0009 (2)
(b)	0.5544 (2)	0.2572 (2)	0.3581 (2)	0.0281 (4)	0.0253 (3)	0.0281 (3)	0.0070 (3)	0.0037 (3)	0.0009 (2)
H(1) (a)	0.267 (2)	0.266 (2)	0.597 (2)	0.067 (4)					
(b)	0.267	0.266	0.597	0.067					
H(2) (a)	0.467 (2)	0.171 (2)	0.344 (2)	0.075 (5)					
(b)	0.467	0.171	0.344	0.075					
H(3) (a)	0.626 (2)	0.201 (2)	0.419 (2)	0.062 (4)					
(b)	0.626	0.201	0.419	0.062					

groups. After averaging Fig. 1(b) is obtained. The peak heights of 0.35, 0.20 and 0.10 Å for the CN, C and N lone-pair peaks respectively are comparable with those obtained in the best room-temperature studies with conventional equipment. The background away from the atoms shows little noise, indicating a satisfactory level of data quality. The deformation density through the Cr atom and four ammine N atoms is given in Fig. 2. The lone pair on the N atom is clearly visible. The density in the N-H bond is not visible because of the bias in the H-atom position obtained in the full-data refinement.

A full discussion of the chemical implications of the deformation density will be given upon completion of the X-ray/polarized-neutron study.

Conclusions

This work clearly shows that given proper precautions accurate diffraction studies can be performed with synchrotron radiation. In particular the reduction of extinction and absorption effects when short-wavelength radiation can be combined with small sample size alleviates one of the main limitations to increased accuracy in diffraction studies. Furthermore the narrowness of the diffraction profile leads to a reduction in the TDS background included in the diffraction peak. Because of this high angular resolution, correction for TDS will be more straightforward, and the reverse procedure of deriving elastic constants from the observed profile should be feasible.

The full power of the high-energy photon beam will be realized when low-temperature equipment has been installed.

This work was supported by grants DMRSC2583 and CHE8403428 from the National Science Foundation. Assistance from the CHESS staff is gratefully acknowledged. We would like to thank Dr K. Tanaka for the growing of the crystals.

APPENDIX A

The unequal step-scan

Many crystals have reflection profiles with a sharp peak but very long tails. With equal steps an appreciable part of the time would be spent on measuring the tails and the background beyond the tails. The following algorithm makes it possible to reduce step size towards the center of the scan.

The algorithm is as follows:

If a scan parameter X is defined as:

$$X = \frac{n-1}{N} - \frac{1}{2}, \quad (\text{A1})$$

where N is the number of steps in the scan, and n is the measuring position number $1 \leq n \leq N+1$, then $-0.5 \leq X \leq 0.5$.

The scan motor is at position P given by

$$P = P_c + WX, \quad (\text{A2})$$

where P_c is the center of the scan and W is the scan width.

To make the positions P non-equidistant X is replaced by X' such that

$$X' = 4X^3, \quad (\text{A3})$$

which means that $-0.5 \leq X' \leq 0.5$; thus the scan width is not changed. However, (A3) gives zero stepsize near the center of the scan. To obtain finite steps in this region 'oddness' is defined as the mixing parameter of normal and odd scans:

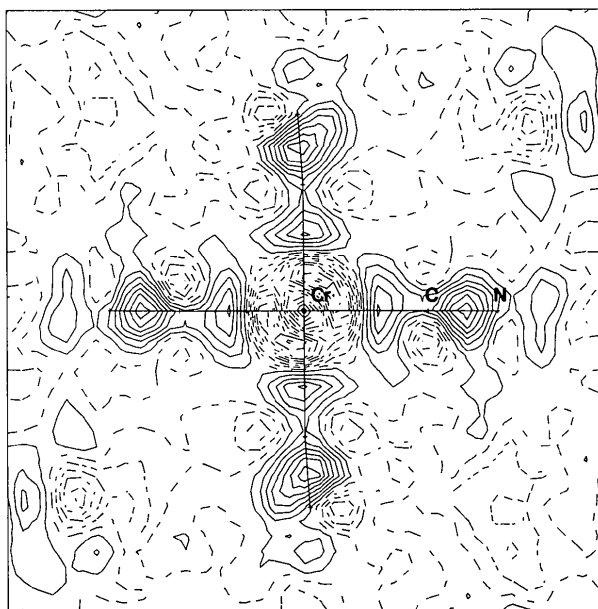
$$X'' = (1 - OD) \times X + OD \times 4 \times X^3,$$

with $0 \leq OD \leq 1$.

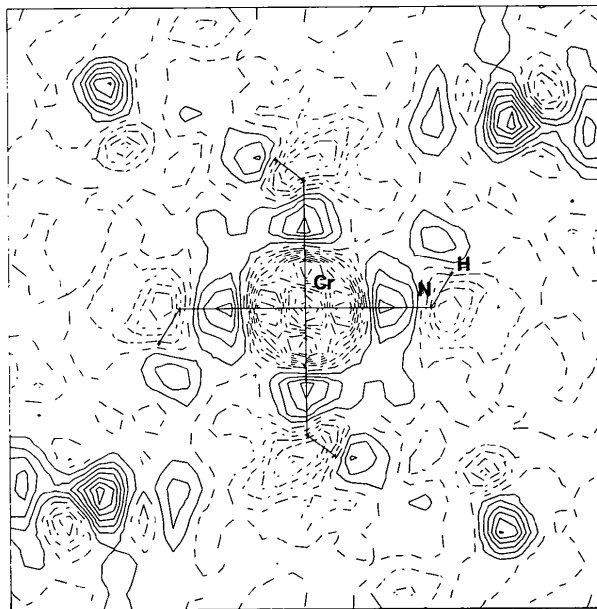
Note that $OD = 0$ gives a normal scan, and that at $X = \pm \frac{1}{2}$ the step size

$$\Delta P / \Delta n = (1 - OD) \frac{W}{N} + 3 OD \frac{W}{N}.$$

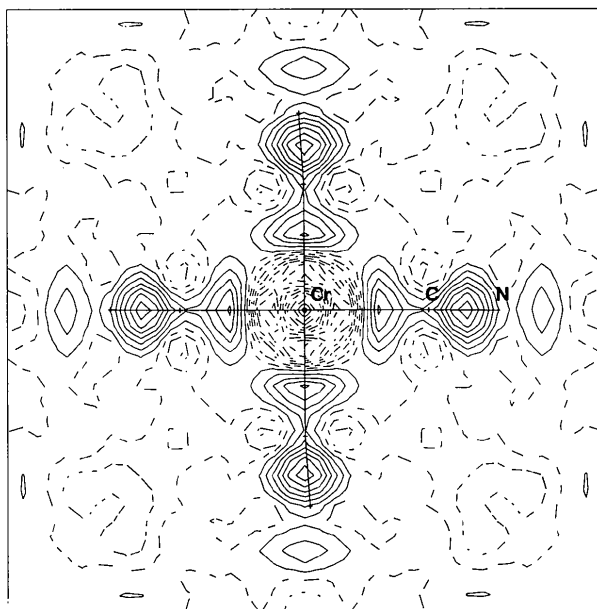
Thus, $OD = \frac{1}{2}$ gives a step-range of $2W/N$ to $W/2N$ and doubles and halves the scan widths in the tails and near the center respectively.



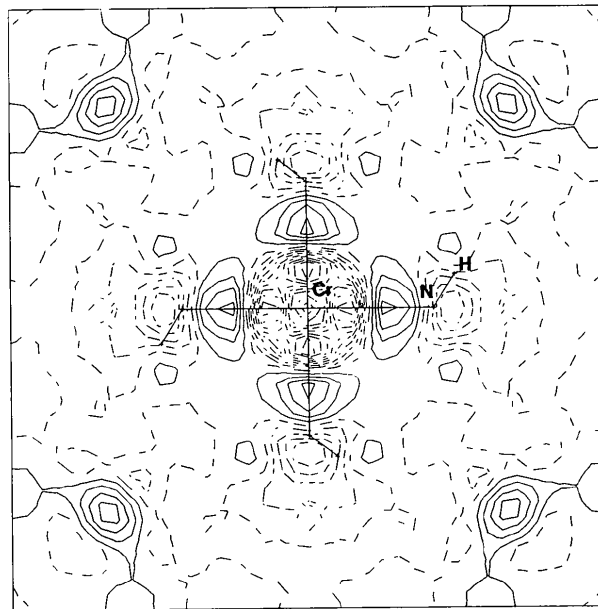
(a)



(a)



(b)



(b)

Fig. 1. $X-X$ deformation maps in the $\text{Cr}(\text{CN})_4$ plane based on parameters from the high-order refinement ($\sin \theta / \lambda > 0.7 \text{ \AA}^{-1}$), including all reflections with $\sin \theta / \lambda < 0.8 \text{ \AA}^{-1}$. Contours at 0.05 e \AA^{-3} , negative contours broken. (a) Before averaging, (b) after averaging over chemically equivalent regions.

Fig. 2. Deformation density map in the plane through the Cr atom and four N atoms of the ammine group. (a) As Fig. 1(a), (b) as Fig. 1(b).

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Acta Cryst. (1986). **B42**, 364-371

Structural Study of CdY₂S₄

BY A. TOMAS, M. GUITTARD AND J. FLAHAUT

*Laboratoire de Chimie Minérale Structurale, associé au CNRS n° 200 (Laboratoire de Physique),
 Faculté des Sciences Pharmaceutiques et Biologiques, Paris-Luxembourg, 4 avenue de l'Observatoire,
 75270 Paris CEDEX 06, France*

AND M. GUYMONT, R. PORTIER AND D. GRATIAS
 CECM, 15 rue Georges Urbain, 94400 Vitry, France

(Received 1 July 1985; accepted 19 November 1985)

Abstract

$M_r = 418.46$, cubic, $Fd\bar{3}m$, $a = 11.216(3) \text{ \AA}$, $V = 1411.0(4) \text{ \AA}^3$, $Z = 8$, $D_m(293\text{K}) = 3.9(1)$, $D_x = 3.94 \text{ Mg m}^{-3}$, $\lambda(\text{Mo } K\alpha) = 0.71069 \text{ \AA}$, $\mu = 20.6 \text{ mm}^{-1}$, $F(000) = 1400$, $T = 293 \text{ K}$, $R = 0.045$ for 105 independent reflections. The crystal can be described as domains with a disordered rocksalt structure, corresponding to the formula Cd₂Y_{4/3}S₄, which grow coherently within ordered domains of spinel structure (98%) of formula CdY₂S₄. In the perturbed NaCl structure, the satellites and linear diffuse streaks along $\langle 111 \rangle^*$ are related to substitutive and displacive disorder in the stacking of atomic planes $\{111\}$.

1. Introduction

Compounds of formula CdL₂S₄, with $L = \text{La-Dy}$, crystallize in the Th₃P₄ structure or, with a smaller cation radius ($L = \text{Ho-Lu}$ and Sc, Y), in the spinel-type structure (Flahaut, Domange & Patrie, 1962; Flahaut, Guittard, Patrie, Pardo, Golabi & Domange, 1965; Flahaut, 1968; Suchow & Stemple, 1963, 1964; Carter, 1972; Tomas, Shilo & Guittard, 1978; Ben Dor & Shilo, 1980). On the basis of a structural determination using an X-ray powder pattern, the ternary sulfide CdHo₂S₄ is reported to have a normal spinel structure with a lattice parameter equal to 11.168 Å (Yim, Fan & Stofko, 1973). On the other hand, Fujii (1972) reports the structure of CdHo₂S₄, with a cell parameter equal to 11.24 Å, as that of an 'intermediate spinel' with only 60% of the Cd cations occupying the tetrahedral 8(a) positions. This ques-

tion is clarified by Bakker, Vollebregt & Plug (1982) who have observed the transition from the spinel-type structure to rocksalt structure by electron microscopy and diffraction. These results show that for $T < 1173 \text{ K}$, CdHo₂S₄ has the spinel structure. For intermediate temperatures, $1173 \text{ K} < T < 1373 \text{ K}$, the spinel structure becomes unstable, Cd²⁺ shifting from tetrahedral to octahedral positions, and transforms gradually into a rocksalt structure, leading to a transition state. The S lattice is distorted by a planar modulation along (111) and linear diffuse streaks along $\langle 111 \rangle^*$ appear in the (110)* diffraction pattern. In this range of temperature, the crystal is assumed to be built from domains of a NaCl-type structure which grow within a matrix of a spinel-type structure. These features explain the increase of the cell parameter found by Fujii. In the same way, the occupation factor of Cd²⁺ on the tetrahedral site comes from the contribution of spinel domains.

In order to obtain additional information on these questions we have studied the structures of CdTm₂S₄, CdYb₂S₄ and CdY₂S₄ by means of X-ray diffraction and electron microscopy. The results concerning CdYb₂S₄ and CdTm₂S₄ are published elsewhere (Tomas, Vovan, Guittard, Flahaut & Guymont, 1985).

2. Experimental

2.1. Preparation

Y₂S₃ is prepared by heating the oxide contained in a graphite crucible, using an induction furnace in flowing H₂S. Single crystals of CdY₂S₄ were prepared