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CCD AREA DETECTORS OF X-RAYS APPLIED TO THE ANALYSIS OF MINERAL STRUCTURES

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ABSTRACT

The recently available CCD (charge-coupled device) area detector for X-rays provides many advantages over a scintillation detector mounted on a serial diffractometer, including 1) improved sensitivity to weak reflections, which permits the study of very small crystals with a sealed-tube laboratory X-ray source, 2) improved resolution, permiting the study of long-axis problems, and 3) reduced data-collection times. The applicability of the CCD detector to the analysis of mineral structures is demonstrated with several examples. The CCD detector provides structure refinements that are comparable to those obtained using a serial diffractometer in a fraction of the time. More significantly, the sensitivity and resolution of the CCD detector permit the successful elucidation of mineral structures that were previously unattainable. As such, the CCD detector will likely revolutionize the acquisition of diffraction data for the analysis of mineral structures.

Keywords: CCD detector, X-ray diffraction, structure analysis, minerals.

SOMMAIRE

Le développement récent d'une nouvelle génération de détecteur de rayons X muni d'une aire couplée à charge (détecteur dit CCD) possède plusieurs avantages par rapport à un détecteur de scintillation installé sur un diffractomètre en série. Parmi ces avantages, on note 1) une sensibilité accrue aux réflexions de faible intensité, ce qui permet l'étude de très petits cristaux avec une source de rayons X à anode scellé courante, 2) une résolution améliorée, ce qui permet l'étude de cristaux dont la période est longue, et 3) un temps de prélèvement des données beaucoup plus court. L'application d'un détecteur CCD à l'analyse de structures minérales est ici illustré par quelques exemples. Le détecteur CCD permet des affinements de structures cristallines tout-à-fait comparables à ceux que l'on peut obtenir avec un diffractomètre en série, ceci dans une fraction du temps de prélèvement des données. Plus important encore, la sensibilité et la résolution du détecteur CCD permettent la solution de structures qui devaient rester sans solution auparavant. Il est clair que l'avènement de détecteurs CCD révolutionnera l'acquisition de données de diffraction nécessaires à la solution de structures de minéraux.

(Traduit par la Rédaction)

Mots-clés: détecteur CCD, diffraction X, analyse de structure, minéraux.

INTRODUCTION

Knowledge and understanding of the crystal structures of minerals are fundamental to the discipline of mineralogy. For more than two decades, the automated four-circle serial diffractometer has been the primary tool for mineral-structure analysis. There have been significant advances in structure-solution software and diffractometer automation, but the process of data acquisition has remained essentially unchanged because of a lack of significant advances in X-ray detector technology. Newly available CCD (charge-coupled device) detectors for X-rays show great promise for the analysis of mineral structures. Experiments undertaken using the CCD detector (*e.g.*, Burns 1997, Kharisun *et al.* 1997) have demonstrated important advantages over the scintillation detector, and suggest that the CCD detector will revolutionize the acquisition of diffraction data needed to study mineral structures. In this contribution, I provide an introduction to the new technology and its likely impact on problems in the Earth sciences.

THE CCD-BASED AREA DETECTOR OF X-RAYS

The CCD detector is an area detector that measures X-ray intensity over slices of reciprocal diffraction space (Fig. 1). The detector collects intensity for many reflections simultaneously, resulting in shorter data-collection times as compared to a serial diffractometer,

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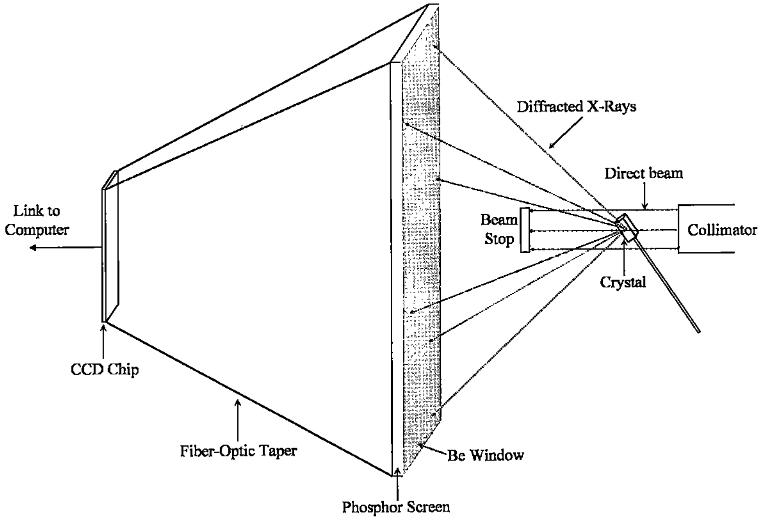

FIG. 1. Schematic illustrating the use of a CCD detector to collect X-ray-diffraction data.

which measures reflections sequentially. The angular range attainable on a single frame depends upon the size of the detector and the crystal-to-detector distance. For example, a CCD detector with a 9 cm diagonal active-imaging area located 5 cm from the crystal can collect reflections over an angular range of 60° 2θ.

The CCD detector contains a phosphor screen located immediately behind a beryllium window; the screen converts incoming X-ray photons into optical photons (Fig. 1). Because of the greater energy of X-ray photons compared to optical photons, hundreds of optical photons are produced for each incident X-ray photon. A fiber-optics taper transmits the optical photons to the CCD chip, where they are converted to stored electrons. The detector is very sensitive to X-rays, permitting the measurement of useful data even for microcrystals that are much too small for acquisition of meaningful data using a serial diffractometer.

Various sizes of CCD chips are available; the most common in usage is a 1 K chip that contains 1024 × 1024 pixels. The 1 K detector provides excellent resolution; for a 1 K CCD chip coupled to a phosphor screen with a 9 cm diagonal active-imaging area, each pixel corresponds to 60 μm on the phosphor screen. The resolution is more than adequate for X-ray-diffraction experiments, even involving structures with very large primitive cells.

The CCD detector measures both strong and weak reflections simultaneously, and is linear until about 90% of the full-well potential is reached, which corresponds to the maximum number of electrons that can be stored on a pixel on the CCD chip. The full-well potential is specific to the CCD chip, but typically is in the range of tens of thousands of counts per pixel. As each reflection falls on many pixels, this corresponds to reflections with more than 1 million counts.

COLLECTION OF DATA USING A CCD DETECTOR

Unlike scintillation detectors, which are used to collect diffraction intensity at discrete points in reciprocal space, the CCD detector allows sensitive simultaneous detection of all data contained in planes of reciprocal space (Fig. 2). The planar aspect of the images of diffraction space collected with a CCD detector facilitates the study of superstructures, twinning, exsolution, and defects, all of which are common in minerals. The CCD detector decreases the time required for the collection of data, as compared to a serial diffractometer, while at the same time providing longer collection-times for individual reflections. Long count-times for individual reflections, together with the sensitivity of the CCD detector, make the detector well suited for studying crystals that are as much as an order of magnitude smaller in all axial dimensions than required for scintillation detectors.

Preliminary evaluation of crystal quality is achieved very quickly using a CCD detector. The detector provides strong diffraction spots for a well-diffracting crystal in ~10 s, and a few exposures at different settings of the crystal rapidly provides an indication of the crystal quality. A series of a few data frames

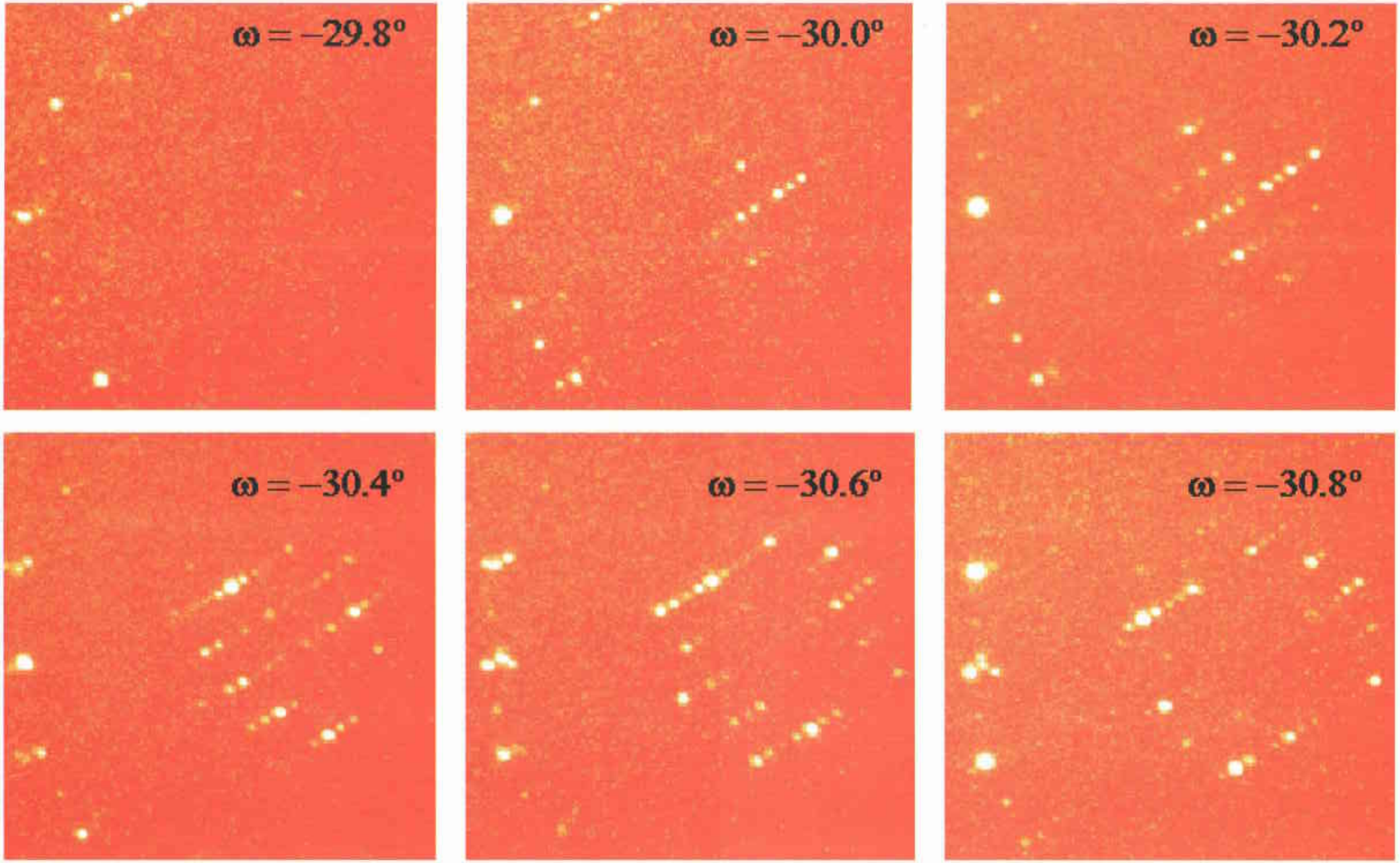

FIG. 2. A series of frames collected for a crystal of vandendriesscheite using a count time of 20 s. Approximately one-fourth of the frame is shown in each case, and corresponds to ~30 to 60° 2θ. Note that each reflection occurs on several frames.

(exposures) at different settings of the detector in positive and negative 2θ space can be used for unit-cell determination, and requires ~15 minutes for a well-diffracting crystal.

The CCD detector is used to build a three-dimensional image of the diffraction intensity by utilizing the large active-imaging area of the detector to collect many closely spaced planes of reciprocal space. Sets of frames are collected with χ and ϕ fixed and with the detector centered at an appropriate 2θ angle for the desired coverage. Counts are accumulated on the detector during rotation of the crystal about a pre-set angular range of ω (the frame width), and each frame is downloaded in digital form to a computer. Portions of six consecutive frames taken from data collected for a crystal of vandendriesscheite (see below) are provided in Figure 2. Note that each reflection occurs in several consecutive frames, thus providing three-dimensional profiles of the reflections. Typical frame-widths are 0.1 to 0.5°, and 10 or more seconds are spent counting for each frame. The data-collection strategy can be independent of the unit-cell dimensions and the orientation of the crystal, in contrast to data collected with a serial diffractometer. This is significant when investigating weakly diffracting crystals, as the unit-cell dimensions and crystal orientation can be derived using the complete data after collection. In the case of a highly absorbing crystal or a crystal that decays rapidly in the X-ray beam, the data-collection strategy can be optimized by taking into account the orientation of the crystal.

All reflections are collected using the same scan-rate when using a CCD detector, in contrast to the intensity-dependent variable scan-rates that are often used when collecting data with a serial diffractometer. Counting statistics dictate that the peak intensities obtained for strong reflections are substantially more precise than those obtained for weak reflections collected at the same scan-rate. This may adversely influence the refinement of the structure of a crystal with many weak reflections, although the CCD detector is much more sensitive to weak reflections than a scintillation detector, in part offsetting effects caused by the scan rate.

The CCD detector permits the collection of a data set with many redundant reflections in a few hours. The redundant reflections improve the statistics of the data and facilitate empirical corrections for absorption of X-rays by the crystal. For example, more than a hemisphere of data can be collected over the range ~0 to ~60° 2θ by using a 9 cm active-imaging area CCD detector positioned at 30° 2θ and a crystal-to-detector distance of 5 cm. Only one detector setting is required, and three sets of frames corresponding to settings of ϕ provide appropriate coverage. If frame widths of 0.3° and 10 s exposures are used, ~1270 frames are required, and the data is obtained in ~5.5 h, regardless of crystal symmetry. Increased resolution for long-axis problems and a reduced background can be achieved by increasing the crystal-to-detector distance, at the expense of necessitating more than one detector setting to obtain appropriate coverage.

Unit-cell parameters are obtained by analyzing a series of frames to locate diffraction peaks. The unit-cell dimensions are used while performing the integration of peak intensities that are contained in the three-dimensional image of reciprocal space. Integration is done using a preset box centered on each reflection, which is chosen on the basis of peak widths in three dimensions. This approach provides better integrated intensities for poor crystals (with ragged peak profiles) than are obtained using a serial diffractometer, because a two-dimensional scan across the peak is used for intensity integration in the latter case.

Examples of the Use of the CCD Detector

Because the applicability of a CCD detector for the analysis of mineral structures is best demonstrated with experimental results, I outline here examples which provide: 1) a comparison of a structure refined with data collected using a scintillation detector and a CCD detector for the same crystal (colemanite), 2) structure results from CCD-detector data collected for a highly absorbing crystal in which the CCD detector is advantageous because of the small size of crystal that is required (curite), 3) structure results from data collected with a CCD detector using a crystal that is too small to be analyzed using a serial detector (edoylerite), and 4) structure results using CCD-detector data collected from a crystal that has an axial length that is too long to be collected using a standard serial diffractometer with Mo radiation (vandendriesscheite). The data collections discussed below were done in the Environmental Mineralogy and Crystal Structures Laboratory at the University of Notre Dame, or in the X-ray Diffraction Laboratory in the School of Chemical Sciences, University of Illinois at Urbana – Champaign. The Siemens SMART (Siemens Molecule Analysis Research Tool) system was used. It consists of a sealed-tube Mo X-ray source, a PLATFORM three-circle goniometer, and a 1 K CCD detector. The diagonal of the active-imaging area of the 1 K detector is 9 cm, and data were collected with 512 by 512 pixel resolution, providing ample resolution for X-ray-diffraction experiments. The crystal-to-detector distance was 5 cm, and three sets of frames were collected for each crystal, with ϕ fixed at 0.0, 88.0 and 180.0°, respectively. The data were collected at room temperature, and the Siemens program SAINT was used for data reduction. Data were corrected for Lorentz, polarization, and background effects. The structures were solved and refined using the Siemens SHELXTL Version 5 system of programs. Scattering curves for neutral atoms, together with anomalous-dispersion corrections, were taken from *International Tables for X-Ray Crystallography, Vol. IV* (Ibers & Hamilton 1974).

Colemanite: a routine structure-refinement

Colemanite, $CaB_3O_4(OH)_3(H_2O)$, forms excellent crystals with low X-ray absorption ($\mu = 10.2$ cm^{-1}). The structure was refined by Burns & Hawthorne (1993) using data collected on a Nicolet *R*3*m* serial four-circle diffractometer with a scintillation detector. The structure has been re-refined on the basis of F^2 using the data of Burns & Hawthorne (1993) for data in the range $3 \leq 2\theta \leq 56.7°$ (for comparison to the CCD-detector data). The model included anisotropic-displacement parameters for all non-H atoms, as well as positional parameters for all atoms. The details of the data collection and refinement are presented in Table 1.

Data were collected for the same crystal of colemanite using the CCD detector. The structure was refined with the model used for the serial-diffractometer data; details of the data collection and structure refinement are given in Table 1.

The data collection for colemanite using the CCD detector required 10% of the time needed by the serial diffractometer. The CCD detector measured approximately twice as many reflections as the serial diffractometer (providing redundancy in the data, which improves the statistics), and the total number of unique observed reflections is similar in each data set (Table 1). Both experiments resulted in similar *R* indices, and the final difference-Fourier maps obtained from each data set are similar (Table 1). A detailed comparison of the refined structures indicates that the two structures are identical, with bond-lengths obtained from both data sets indistinguishable within one standard deviation.

Curite: a structure containing high absorbers

Curite, a Pb uranyl oxide hydrate, has a linear-absorption coefficient for Mo X-rays of 670 cm^{-1}. The structure of curite reported by Taylor *et al.* (1981) is based upon data collected on a serial diffractometer for a crystal with dimensions $0.136 \times 0.01 \times 0.01$ mm, with a final *R* of 9% for 967 observed reflections.

The high sensitivity of the CCD detector permits the collection of data for very small crystals, thus reducing the effects of absorption. A crystal of curite with dimensions $0.08 \times 0.05 \times 0.03$ mm was selected for data collection; the details of the experiment and structure refinement are presented in Table 2. Owing to the small size of the crystal, the total data-collection required 45 h. However, the structure model, which included the positions of all atoms, anisotropic-displacement parameters for the cations, and isotropic-displacement parameters for the anions, provided an excellent refinement, with an *R* of 3.9%. Details of the structure will be presented elsewhere (Burns, in prep.).

TABLE 1. MISCELLANEOUS INFORMATION PERTAINING TO DATA COLLECTIONS AND CRYSTAL STRUCTURE REFINEMENTS FOR VARIOUS MINERALS

Colemanite* (serial diffractometer)			
a (Å)	8.712(2)	Crystal size (mm)	0.24x0.08x0.20
b (Å)	11.247(2)	Total ref.	1819
c (Å)	6.091(1)	Unique ref.	1392
β (°)	110.12(2)	Ref. with $\lvert F_O \rvert \geq 4\sigma_F$	1248
μ (cm^{-1})	10.2	R_{INT}	-
Space group	$P2_1/a$	Absorption correction	Empirical
2θ range collected	0-56.7°	$R_{azimuthal}$	2.1→1.8
Collection time	60 h	Final *R* (obs. ref.)	3.07
		Final *R* (all data)	3.53
		Difference-Fourier peaks	0.36/-0.75 e/Å^3
Colemanite (CCD detector)			
a (Å)	8.7315(7)	Crystal size (mm)	0.24x0.08x0.20
b (Å)	11.2653(9)	Total ref.	3398
c (Å)	6.1004(5)	Unique ref.	1327
β (°)	110.120(1)	Ref. with $\lvert F_O \rvert \geq 4\sigma_F$	1235
μ (cm^{-1})	10.2	R_{INT}	2.2
Space group	$P2_1/a$	Absorption correction	Empirical
Detector position	30°2θ	$R_{azimuthal}$	3.10→2.08
2θ range collected	0-56.7°	Final *R* (obs. ref.)	2.96
Frame width	0.3°	Final *R* (all data)	3.19
Count time	10 s	Difference-Fourier peaks	0.33/-0.80 e/Å^3
Collection time	6 h		
Curite			
a (Å)	12.5403(1)	Crystal size (mm)	0.08x0.05x0.03
b (Å)	13.0170(4)	Total ref.	7530
c (Å)	8.3955(3)	Unique ref.	1573
μ (cm^{-1})	670	Ref. with $\lvert F_O \rvert \geq 4\sigma_F$	1454
Space group	*Pnam*	R_{INT}	3.1
Detector position	25°2θ	Absorption correction	Empirical
2θ range collected	0-55°	$R_{azimuthal}$	12.9→5.5
Frame width	0.15°	Final *R* (obs. ref.)	3.90
Count time	60 s	Final *R* (all data)	4.37
Collection time	45 h	Difference-Fourier peaks	4.81/-2.67 e/Å^3
Edoylerite**			
a (Å)	7.5283(4)	Crystal size (mm)	0.04x0.005 x0.002
b (Å)	14.8325(8)		
c (Å)	7.4629(4)	Total ref.	3760
β (°)	118.746(1)	Unique ref.	1470
μ (cm^{-1})	648	Ref. with $\lvert F_O \rvert \geq 4\sigma_F$	1193
Space group	$P2_1/c$	R_{INT}	6.8
Detector position	25°2θ	Absorption correction	Gaussian
2θ range collected	0-55°	Final *R* (obs. ref.)	7.9
Frame width	0.1°	Final *R* (all data)	10.3
Count time	120 s	Difference-Fourier peaks	2.96/-2.77 e/Å^3
Collection time	130 h		
Vandendriesscheite***			
a (Å)	14.1165(6)	Crystal size (mm)	0.16x0.10x0.045
b (Å)	41.378(2)	Total ref.	53,227
c (Å)	14.5347(6)	Unique ref.	10,257
μ (cm^{-1})	443	Ref. with $\lvert F_O \rvert \geq 4\sigma_F$	4918
Space group	*Pbca*	Absorption correction	Gaussian
Detector position	30°2θ	Final *R* (obs. ref.)	12.1
2θ range collected	0-56.5°	Difference-Fourier peaks	4.01/-4.43e/Å^3
Frame width	0.2°		
Count time	10 s		
Collection time	7 h		

*from Burns & Hawthorne (1993)

**from Burns (1998)

***from Burns (1997)

Edoylerite: the structure of a microcrystal

Many minerals only form microcrystals that are too small to permit the collection of data using a serial diffractometer equipped with a sealed-tube X-ray source. Before the introduction of the CCD detector,

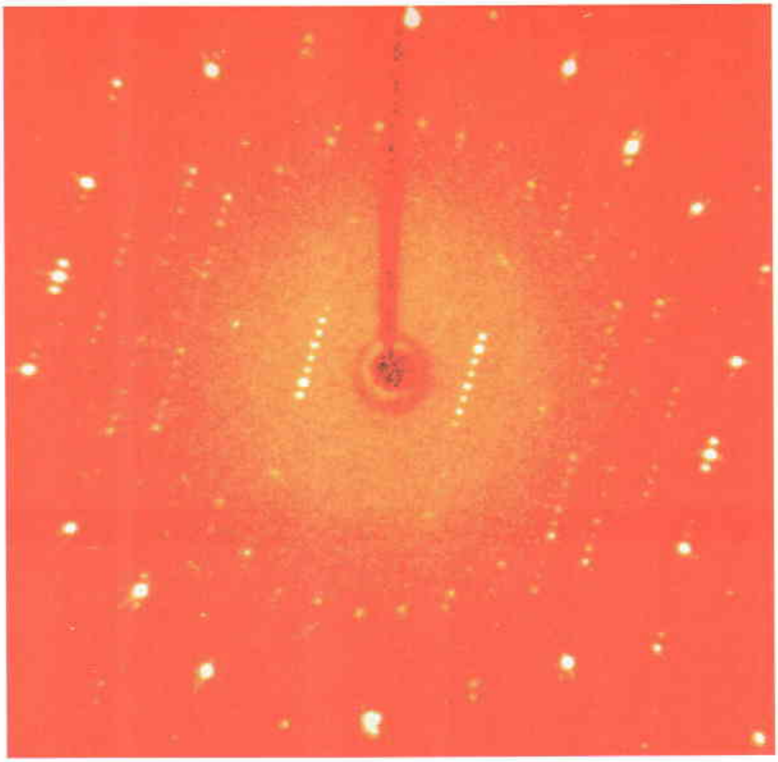

FIG. 3. The intensity recorded along the [101] zone-axis using the CCD detector for a crystal of vandendriesscheite. The frame was accumulated for 120 s while rotating the crystal through 7° about ω. The closely spaced spots result from the 41.3 Å *b* unit-cell length.

the structures of microcrystals could only be studied using intense sources of radiation (synchrotron) or powder-diffraction methods. Synchrotron beam-time is very expensive and is in limited supply, but can be counted on to provide excellent structural data for microcrystals, whereas X-ray powder-diffraction data seldom provide sufficient resolution for the solution of a crystal structure.

Although edoylerite, $Hg_3CrO_4S_2$, forms fairly large crystals (~0.5 mm in length, Erd *et al.* 1993), the CCD detector showed that they are not single crystals. Therefore, data were collected on a very small crystal with an estimated volume of 400 μm^3. The details of the data collection and structure refinement are provided in Table 1. Initially, a hemisphere of data was collected, with exposures of 30 s and a frame width of 0.2°. The data were sufficient to solve the structure, but the final *R* was 10.5%. A second data set was collected with an exposure time of 120 s and a frame width of 0.1° in 130 h, giving a scan-rate of 0.05° per minute. The longer count-time substantially improved the refinement; a model that included the positional parameters and anisotropic displacement of all atoms refined to an *R* of 7.9%. The details of the structure of edoylerite will be reported elsewhere (Burns 1998).

Vandendriesscheite: a long-axis problem

Vandendriesscheite, $Pb_{1.57}[(UO_2)_{10}O_6(OH)_{11}](H_2O)_{11}$, is a common constituent of the oxidized portions of many U deposits, but its structure remained unknown because of its large primitive unit-cell (Table 1). The *b* unit-cell parameter is ~41.3 Å, which causes problems for collection of data using a serial diffractometer and Mo X-radiation, because the estimation of background counts is seriously affected by peak overlap. The CCD detector resolved the long axis (Fig. 3), and the data (Table 1) were adequate to solve and refine the structure. The details of the structure are reported by Burns (1997).

Summary of examples

The experiments described above illustrate the capabilities of the CCD detector for the analysis of mineral structures. For routine structure-solution or structure refinement of materials with low symmetry and either high or low absorption, data collected using a CCD detector give excellent results that are comparable to those obtained using data sets collected with a serial diffractometer equipped with a scintillation counter, with the advantage that the data-collection time is greatly reduced if a CCD detector is used. This will be especially significant in the case of crystals that are unstable during lengthy exposure to X-rays. However, the most significant advantages of the CCD detector are realized where the crystals are very small or where the unit cells are very large. In these cases, the CCD detector can be used to obtain structure solutions for material that are intractable using a serial diffractometer and scintillation counter.

DISCUSSION

The CCD detector provides many advantages over a serial diffractometer equipped with a scintillation counter, and as such, it will probably become widely used for the determination of mineral structures. Perhaps the largest impact of the CCD detector in mineralogy will be an improvement of our understanding of low-temperature minerals, and the complex relationship between their structure and paragenesis. In particular, the associations of low-temperature minerals that occur in the weathered zones of many ore deposits as well as mine tailings challenges our understanding of mineralogy. The key to modeling such complex assemblages is an understanding of the relationship between mineral stabilities and crystal structures. Such an approach is now becoming possible for low-temperature minerals, with the determination of many crystal structures in recent years. However, many low-temperature minerals occur as small crystals that are commonly intergrown, making the determination of their structures difficult. *The CCD detector is well suited to studies of such problems.*

Petrological studies typically involve chemical and isotopic analyses of minerals and rocks, without the detailed analysis of the crystal structures of the constituent minerals. Details of the crystal structures could, however, provide useful information pertaining to the geological history of the rock. For example, cation ordering in minerals is related to cooling history, and is prerequisite information for thermodynamic models. However, the refinement of a crystal structure for feldspar or amphibole, for example, requires several days of instrument time when using a conventional serial diffractometer. The CCD detector provides high-quality data in a fraction of the time, regardless of the symmetry of the crystal, with data collection for a strongly diffracting crystal requiring no more than a few hours. Thus, *it is now possible to include crystal-structure analysis of rock-forming minerals in petrological studies*, with the refinement of several dozen structures attainable in a reasonable timeframe.

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