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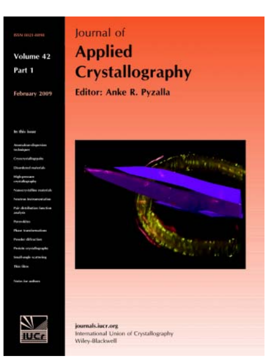

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Computer-controlled high-temperature single-crystal X-ray diffraction experiments and temperature calibration

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This work provides a simple way to operate and calibrate single-crystal gas flow heaters that use heating currents up to 10 A. Devices used for this task are an I-7019R data acquisition interface (ICP DAS Co. Ltd, Hsinchu, Taiwan) and an SDP-2210 power unit (Manson Engineering Industrial Ltd, Hong Kong; I_{max} = 10 A, V_{max} = 20 V), which are both connected to one computer. The presented open source software *htcontrol* (http://htcontrol.sourceforge.net) is able to control the heating current and to monitor the temperature, which allows automated calibrations. In particular, this work targets Stoe IPDS II diffractometer systems with a Heatstream high-temperature (HT) device. The extra hard- and software enables computer-controlled HT data collection series, which are performed utilizing the *WinXpose* software (Stoe & Cie GmbH, Darmstadt, Germany). New developments in *WinXpose* allow non-interactive data collections, which are controlled by means of an XML file specifying the measurement conditions.

1. Introduction

As a result of increasing interest in non-ambient experimental conditions in X-ray crystallography, many crystallographic laboratories operate equipment for high-temperature (HT) single-crystal diffraction studies. For an overview of different heater designs and their application see Lindley (2004), Peterson (1992) and Shaikh (2007), and references therein. Although based on a few main design principles, many of these devices are home-made and unique.

The development presented here can be applied to gas flow heaters that use a constant flow and a DC power unit (up to 10 A) to provide electric current to the heating device; one such heater is the Heatstream (Stoe & Cie GmbH, Darmstadt, Germany) device (see Fig. 1), which is available for the IPDS diffractometers. The Heatstream furnace is based on the work of Böhm (1995) and Scheufler (1996). It uses a hot N_2 gas stream to heat the crystal under investigation up to 1000 K. The geometry of the IPDS II and 2T goniometers allows a vertical flow of the hot N_2 gas stream, owing to the fact that the device is mounted on the ω axis underneath the sample position. In combination with a constant gas flow, regulated by a mass flow controller (Model MFC-5108, Kobold Messring GmbH, Hofheim, Germany) and constant heating power, this setup ensures excellent temperature stability (less than $\pm$1 K). Unfortunately, the originally provided power supply for the Heatstream device does not allow any other than manual interaction to change the temperature. As a consequence, temperature calibration and extensive HT data collection are potentially very labour intensive. To gain software-based access to HT experiments, three requirements have to be fulfilled: (1) control over the power unit, (2) accessibility of digital temperature data and (3) the possibility to perform data collections. Whereas (1) and (2) can be achieved using additional hardware, (3) needs an interface between the HT controlling software and the existing software for data collection. To account for (1) and (2) a new data acquisition module is connected to the computer for temperature readings, and the power supply of the furnace is exchanged with a model that allows control by a computer. The amount of investment was approximately 600 euros. The devices are connected *via* serial ports to the Windows PC controlling the diffractometer. Therefore, all tasks are operated from one computer. (3) is made possible by a new development in the *WinXpose* software (Stoe & Cie, 2008) for the IPDS II and 2T diffractometers, which allows the data collections to be controlled/started by third-party software, such as the presented open source HT controlling software *htcontrol*.

htcontrol provides a set of commands that allow the user to program a series of HT data collections or calibration tasks. Even without the option to conduct automated data collections (*e.g.* Heatstream-equipped IPDS I[1] diffractometers), the described setup may significantly ease HT work, especially calibrations.

2. Hardware

2.1. Data acquisition device

The data acquisition module I-7019R-CR (ICP DAS Co. Ltd, Hsinchu, Taiwan) offers an eight channel analog-to-digital converter for digital readout of thermocouples (TCs), voltages and currents. Four of the input channels are used to connect TCs. One of the input channels is connected to the TC at the sample position, which is used for the calibrations (provided by Stoe). The second input channel is used to read the temperature of the Heatstream device by means of its internal TC. Two more type K TCs are used to monitor the

[1] A further improvement for IPDS I systems by means of an adjustable mount for the furnace was described by Wendschuh *et al.* (2008).

ambient temperature and the temperature within the closed diffractometer box. Furthermore, the I-7019R-CR device offers a built-in sensor to deliver a temperature for the internally performed cold junction compensation. All of the temperatures can be accessed directly by a computer, using the I-7520A-CR (ICP DAS Co. Ltd, Hsinchu, Taiwan) bus converter (offers a RS232 connection) and the well documented DCON protocol (ICP DAS, 2006*a*,*b*). The aforementioned Kobold mass flow controller offers a voltage output linear to the N_2 gas flow rate (Kobold Messring, 2001). This voltage is also connected to one of the input channels of the I-7019R-CR and used to monitor the gas flow.

Except for the wiring no further modifications to the system are needed.

2.2. Power unit

The SDP-2210 switching mode programmable DC regulated power supply (Manson Engineering Industrial Ltd, Hong Kong) was chosen to provide the Heatstream furnace with heating current. It delivers up to 200 V A at a maximum of 9.99 A and can be fully controlled by a computer connected *via* an RS232 interface. The command set is documented (Manson Engineering Industrial, 2004) and communication is easy to implement.

3. Software

3.1. htcontrol

The software *htcontrol* is written in the Perl programming language and has been developed to run on the Cygwin platform (http://www.cygwin.com), which can easily be installed on the Windows XP computer controlling the diffractometer. It also runs without significant modifications on Linux systems. *htcontrol* implements all needed communication with the I-7019R-CR and the SDP-2210 and offers flexible methods to perform temperature changes, logging and calibrations. Temperature changes can be achieved with defined rates. Data collections are performed by external software (native software of the diffractometer platform). In order to allow automated HT data collection series, the measurements have to be initiated by *htcontrol*. So far, *htcontrol* has the ability to call *WinXpose* (Stoe & Cie, 2008) to execute data collections. Consequently, high-temperature data collection series without manual intervention are possible on IPDS II diffractometers. For other diffractometer systems this is not yet possible. Assuming that there is a way to start data collections with pre-defined parameters without user-interaction, corresponding commands can be implemented in *htcontrol* to allow the use of other diffractometers. *htcontrol* can be invoked with commandline parameters for short operations, or it can execute comprehensive command lists for long HT measurements or calibrations. All operations, temperatures and power settings are logged. Furthermore, alarm conditions can be detected; exceeding temperature or power limits will shut down the heating power, as will N_2 gas flow failure.

htcontrol is published under the GNU General Public License, allowing users to adapt it to their particular needs, such as other diffractometer systems or differing hardware (*e.g.* other power units, cooling devices *etc.*). The software, including documentation and setup details, can be obtained from the author or from http://htcontrol.sourceforge.net.

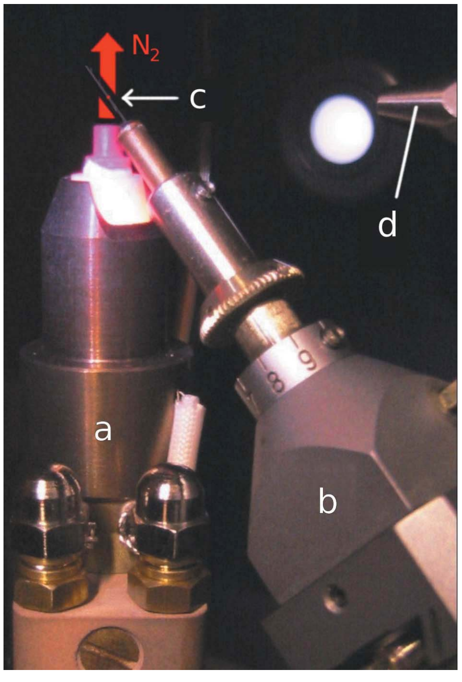

Figure 1
High-temperature sample environment with a Stoe Heatstream device (a) on an IPDS II diffractometer at *ca* 1100 K. The crystal (c) – embedded in an SiO_2 capillary – is placed in the hot nitrogen gas stream. The relative position between the furnace (a) and the goniometer head (b) is not changed during the data collection. In the upper right corner the X-ray collimator (d) can be seen.

3.2. *WinXpose*

The software *WinXpose* (Stoe & Cie, 2008) controls all needed operations in order to perform data collections on IPDS II and 2T diffractometers. Its most recent version adds a new feature: non-interactive measurements. Parameters and conditions regarding the data collection can be defined in a communication file. The communication file uses the XML syntax, which was chosen because of its well defined, easy to understand syntax, its platform independence and its widespread distribution. Nearly every modern programming or script language allows the creation of XML files. The structured XML syntax also allows the inclusion of data and information designed for other programs, for example for post-processing the measured data, without interfering with the data used by *WinXpose*. The XML file is used for bidirectional communication; status reports and error messages of *WinXpose* are written into the file, allowing external software to react to hardware problems or other interruptions.

In practice, an external program, like *htcontrol*, writes a communication file containing all parameters needed to perform the measurement. Subsequently, it calls *WinXpose*, which will read and process this file. After the measurement conditions have been validated, *WinXpose* starts the data collection automatically without any user interaction. When the measurement has been completed *WinXpose* will write a status report (*e.g.* `Status = "done"`) into the communication file. By monitoring this file the external program is able to detect whether the data collection has finished successfully.

4. Calibration

The true temperature at the sample position cannot be measured with a TC during the X-ray diffraction experiment, unless the TC is placed in the very close vicinity of the sample. However, this would lead to problems because of the scattering of the TC. Therefore, a different technique has to be utilized. Owing to the excellent temperature stability of the described experimental layout, the temperature at the sample position can be determined as a function of the heating current before or after the data collection. To measure the temperature at the sample position, a very small type K TC is used (Stoe & Cie GmbH, Darmstadt, Germany), which can be placed at the zero point of the goniometer. The measured temperatures are susceptible to deviations, such as heat loss by radiation, conduction by the TC's wires (Scheufler, 1996), deviations of the TC measurement (*e.g.* wrong cold junction compensation) and possible misalignment of the furnace relative to the sample position. Whereas careful alignment of the furnace and calibration of the TC temperature can rule out the latter two issues, heat conduction of the TC's wires can only be minimized by using very thin wires. Furthermore, the wires should be arranged in such a way that they do not leave the hot gas stream through a high-gradient region.

During the X-ray diffraction experiment additional deviations may be introduced by the mounting of the sample. For HT experiments, single crystals are normally fixed in a capillary made from fused quartz. It has to be assumed that the real temperatures of the sample (embedded in the capillary) are smaller than the temperatures obtained by direct measurement with the TC, owing to insulation effects and heat conduction of the capillary. To account for these deviations two methods can be employed: the TC used for the calibration has to be placed in a capillary, whose size and mounting should match the experimental conditions as closely as possible, or observations of well known phase transitions can be used to determine the deviations. We use powders of several compounds embedded in fused quartz capillaries as used for mounting of single crystals. The power settings of the furnace at the phase transitions are then checked by the evaluation of a series of powder frames, which is performed using the *Poly* software (Stoe & Cie, 2004). The series of powder frames are measured with a step-by-step increase of the power settings (the smallest possible steps with the SDP-2210 are 0.01 A), across the temperature range to be examined. This can be carried out automatically, controlled by *htcontrol* (example programs are included in the software documentation).

In the range from room temperature up to 1000 K we found the following phase transitions to be useful (and easy to identify from powder diagrams) for calibration: the $\alpha \rightarrow \beta$ transition of KNO_3 at 403 K (Breuer & Eysel, 1982; Christensen *et al.*, 1996); the $\beta \rightarrow \alpha$ transition of Ag_2SO_4 at 702 K (own DTA measurement[2]); the $\beta \rightarrow \alpha$ transition of K_2SO_4 at 857 K (own DTA measurement[2]); the $\beta \rightarrow \alpha$ transition of K_2CrO_4 at 942 K (Charsley *et al.*, 1993; Choi, 1999).

In practice, the temperature at the sample position is measured by means of the provided TC as a function of the heating current set by the power unit. Use of the set heating current includes deviations from the actual output heating current. The result is a function that gives a good qualitative description of the temperature curve. The temperature curve should be sampled on a fine grid of current settings. For each step the system should be allowed to equilibrate before recording of the temperature. This procedure can be computer-controlled using *htcontrol*. The recorded temperature curve can be characterized by a higher-order polynomial function. Its parameters are obtained from a fit. The same function is subsequently fitted to a data set of known phase transitions, which are observed by *in situ* experiments as described above. For the latter fit only the coefficients of the constant and linear terms of the polynomial function are used. This ensures that the characteristics of the function are not significantly changed, while constant and linear deviations of the TC measurements are accounted for.

5. Conclusions

The described additional equipment and software provide a powerful tool for temperature-dependent structural studies. This tool also makes temperature calibration easier, leading to better calibration results. Furthermore, it may help to preserve the furnace, owing to the use of defined temperature rates to change power settings, in contrast to coarse manual changes. Safety is improved through the monitoring of temperatures, power settings and nitrogen flow.

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[2] Phase transition temperature determined on a Seteram Setsys Evolution 2400 using a TGA-DTA1600 transducer with Pt/PtRh10% TCs at a rate of 5 K min^{-1}.