Short Communications

The calibration of microthermostats for X-ray measurements on crystals. By J. C. McC.

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In the development of high- and low-temperature microthermostats for X-ray work, several methods have been used to estimate the specimen temperature (Ubbelohde & Woodward, 1946; Hume-Rothery & Strawbridge, 1947; Pearson, 1954). A very direct method of calibration is to measure the lattice spacing of some substance placed in the operating position in the thermostat, and for which the lattice spacings are accurately known in the desired temperature range. The number of substances suitable for this type of measurement is limited. The substance used should have a large coefficient of thermal expansion so that a small change in temperature is readily detected from the change of Bragg angle. To shorten exposure times there should be a fairly intense X-ray reflexion of Bragg angle about 80° at room temperature. In general, a compromise has to be made between large thermal expansion and large Bragg angle. If both are too large, high-Bragg-angle reflexions may be lost at extreme temperatures, and the calibration range is limited.

Nix & McNair (1941, 1942) have made accurate measurements of the thermal expansion of a wide range of metals. Their values for aluminium have been applied to X-ray work by Pearson (1954), who used them for temperature calibration. The relatively low value of the coefficient of expansion of aluminium ($18 \cdot 35 \times 10^{-6}$/°C.) means, however, that only a very small shift in the position of the reflexion is produced for an appreciable temperature interval, and this increases the difficulty of accurate calibration.

Present work shows that pure lead has a number of advantages for calibrating microthermostats. It can be obtained in a high state of purity; it has a large coefficient of expansion (27×10^{-6}/°C.) and an intense X-ray reflexion (620) of Bragg angle 79° with Cu $K\alpha_1$ radiation (22° C.). Nix & McNair have previously studied the thermal expansion of lead in the temperature region $-188°$ C. $\rightarrow +25°$ C., but, since their measurements were made by an interferometric method on the bulk metal, it was considered desirable to determine accurately the thermal expansion of the crystal lattice for comparison with their values.

Preliminary X-ray photographs at room temperature and at liquid-nitrogen temperatures (using the method of Lonsdale & Smith (1941)) showed that the (620) reflexion shifted by about 5 mm. (on a 7 cm.-radius camera) for a temperature interval of 215° C. Since the position of the reflexion could be measured to 0·01 mm. by means of a modified Hilger photometer (to be described in a later publication) this means that temperature can be estimated by this means to approximately 0·5° C.

The lead used in this experiment was Johnson-Matthey lead foil of 99·99% purity. One junction of a copper/eureka thermocouple was embedded in a sample of this, and the whole was mounted on a goniometer head as shown in Fig. 1. This set-up closely simulated the operating position for single-crystal work. The thermocouple leads were wrapped round the lead several times to minimize heat conduction errors. Calibration of the thermocouple was first carried out with the lead specimen attached, and all subsequent temperature measurements were made with the same specimen as in this calibration. Fixed points used for calibration were:

	Temperature (°C.)	Observed e.m.f. (mV.)
Freezing Hg	$-38\cdot87$	1·290
Solid/gaseous CO_2 (760 mm. pressure)	$-78\cdot51$	2·504
Boiling O_2 (760 mm. pressure)	$-183\cdot00$	4·862

The equation for the e.m.f. was calculated to be

$$E = 0 \cdot 03395409t - 0 \cdot 000014171t^2 - 0 \cdot 0000001428t^3 .$$

X-ray photographs were next taken of the specimen in the operating position at four different temperatures, $+22\cdot00$, $-45\cdot44$, $-115\cdot00$ and $-183\cdot07$ °C.

The two intermediate temperatures were obtained by blowing cold dry nitrogen over the specimen in a manner previously described (Ubbelohde & Woodward, 1946). The lowest temperature was obtained by a liquid-

Table 1. *Bragg reflexions from pure lead at different temperatures*

Temperature (°C.)	$d_{620} = \left(\dfrac{\lambda}{2\sin\theta}\right)_{\alpha_1}$ (Å)	Mean deviation	$d_{620} = \left(\dfrac{\lambda}{2\sin\theta}\right)_{\alpha_2}$ (Å)	Mean deviation	Mean d_{620} (Å)
$+ 22\cdot0$	0·78307	0·00006	0·78290	0·00009	0·78298
$- 45\cdot44$	0·78157	0·00013	0·78148	0·00019	0·78153
$-115\cdot00$	0·78008	0·00012	0·77986	0·00007	0·77997
$-183\cdot07$	0·77866	0·00012	0·77853	0·00014	0·77860

oxygen drip. Photographs were taken on a Varney–Ubbelohde multiple-exposure spectrometer of 7 cm. radius and the position of the 620 reflexion was measured against a platinum standard (calibrated against silver,
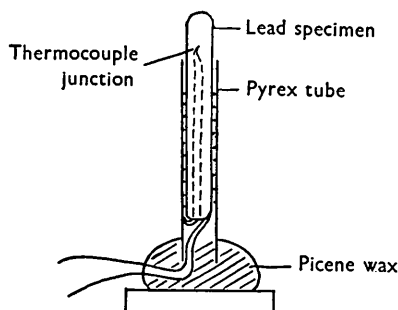

Fig. 1.

$a = 4.0775$ Å). The specimen was oscillated during exposure, since it could not be rotated on account of the attached thermocouple wires. Six film records (two sides each) were obtained in order to assess the scatter of the measurements. Table 1 gives the observed spacings of the 620 plane at the different temperatures.

Cu $K\alpha$ radiation was used throughout, and the constituent wavelengths were taken as

$$\lambda(\alpha_1) = 1.5405 \text{ Å}, \quad \lambda(\alpha_2) = 1.5443 \text{ Å}.$$

A plot of these spacings against temperature gives

$$d_{620} = 0.78251 \text{ Å} \quad \text{at} \quad 0° \text{ C.},$$

$$\frac{1}{d} \cdot \frac{d(d)}{dt} = 27.48 \times 10^{-6}/°\text{C.} \quad \text{at} \quad 0° \text{ C.}$$

The spacing of the 620 plane is related to the cubic cell edge a by the formula $d_{620} = a/2\sqrt{10}$ and thus gives a value of the axial length of lead at 0° C. of 4.949 Å. The value given in the *Handbook of Chemistry and Physics* is 4.951 Å. Using the above d_0's, values of $\Delta d/d_0$ were worked out, and in Fig. 2 these are plotted against temperature. The values of Nix & McNair are also shown. Agreement is very satisfactory, thus providing a useful check on two independent methods.

Table 2

Temperature (°C.)	d_{620} (Å)	Temperature (°C.)	d_{620} (Å)
−180	0.77862	−60	0.78120
−160	0.77905	−40	0.78163
−140	0.77948	−20	0.78206
−120	0.77991	0	0.78251
−100	0.78034	20	0.78293
− 80	0.78077		

For calibration of temperatures by means of pure lead, smoothed values may be used, as in Table 2. Alternatively, one may use the computed equation for the variation of

spacing with temperature. By the method of least squares this has been found to be

$$d_{620} = 0.77662 + 0.000021520t,$$

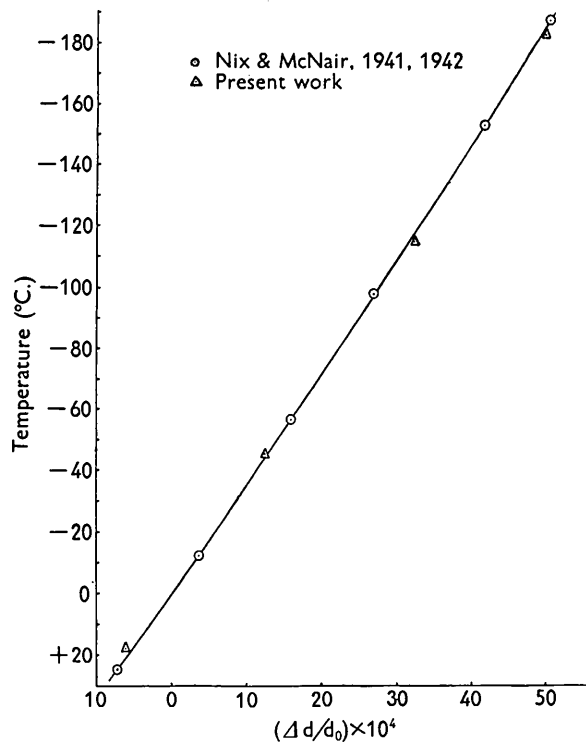where t is the temperature in °K.

Fig. 2.

More sensitive scales of expansion can be based on pure resublimed iodine, which has a high coefficient of expansion of about $84 \times 10^{-6}/°\text{C}$. The thermal expansion normal to the plane of p-nitroaniline can also be used, for which α is about $150 \times 10^{-6}/°\text{C}$. (McKeown, Ubbelohde & Woodward, 1951). However, these crystals, whilst permitting the use of very open scales, are inconvenient for general calibrations extending over a wide range of temperatures.

References

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