

APPENDIX

Total TDS intensity for
slower-than-sound neutrons ($\beta > 1$)

Referring to Fig. 4, we need to integrate the differential cross-section $\left(\frac{d\sigma(\mathbf{q})}{d\Omega}\right)^{(1)}$ over all modes with wave-

vectors \mathbf{q} terminating on the surface of the ellipsoid.

Considering first the modes \mathbf{q}_1 and \mathbf{q}_2 belonging to the same scattering direction \mathbf{k} , we find using equation (6) that

$$\frac{d\sigma(\mathbf{q}_1)}{d\Omega} + \frac{d\sigma(\mathbf{q}_2)}{d\Omega} = \frac{NQ^2}{m} \frac{k_B T}{c_s^2} F(\mathbf{Q})^2 \cdot \frac{\beta}{\eta^2 \sqrt{1 - (\beta^2 - 1) (\eta_{\perp}/\eta_{\parallel})^2}}.$$

Here η_{\parallel} , η_{\perp} are the projections of the vector $\boldsymbol{\eta}$, joining the reciprocal lattice point to the Ewald sphere, along and perpendicular to the scattering direction. By taking the \mathbf{q} vectors in pairs the integration over the ellipsoid is reduced to an integration over a circle of radius R , representing the projection of the ellipsoid on the Ewald plane. The total one-phonon cross-section for a given setting of the crystal is therefore

$$\sigma_1 = \frac{NQ^2}{m} \frac{k_B T}{c_s^2} F(\mathbf{Q})^2 \int_0^R \frac{\beta}{\eta^2 \sqrt{1 - (\beta^2 - 1) (\eta_{\perp}/\eta_{\parallel})^2}} \cdot 2\eta_{\perp} d\eta_{\perp} \cdot \frac{1}{k_0^2}.$$

Acta Cryst. (1970). A26, 401

The Elastic Constants of the Triclinic Crystals Ammonium and Potassium Tetroxalate Dihydrate

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(Received 30 December 1969)

In the triclinic crystals ammonium and potassium tetroxalate dihydrate 34 and 31 sound velocities respectively were measured by means of the diffraction of light by ultrasonic waves. From these velocities the 21 independent components of the elastic tensor were calculated. Thus, the method first tested by Haussühl & Siegert on $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ was successfully applied to two other triclinic crystals. The compounds under investigation were found to exhibit an extremely high elastic anisotropy.

Introduction

The elastic behaviour of triclinic crystals is described by a fourth-rank tensor containing 21 independent components. The determination of these 21 constants from measurements of sound velocities involves, apart

Putting $\sin x = \frac{\eta_{\perp}}{\eta_{\parallel}} (\beta^2 - 1)^{1/2}$,

$$\int_0^R \frac{\eta_{\perp} d\eta_{\perp}}{\eta^2 \sqrt{1 - (\beta^2 - 1) (\eta_{\perp}/\eta_{\parallel})^2}} = \frac{1}{\beta} \tanh^{-1} \left(\frac{1}{\beta} \right),$$

so that finally

$$\sigma_1 = \frac{NQ^2}{m} \frac{k_B T}{c_s^2} F(\mathbf{Q})^2 2k_0^2 \tanh^{-1} \left(\frac{1}{\beta} \right).$$

Thus σ_1 increases from nothing at very long neutron wavelengths ($\beta \gg 1$) to a maximum at the critical wavelength, $\beta = 1$. It is independent of the deviation, $\Delta\theta$, of the crystal from the Bragg setting.

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from a larger experimental expenditure, severe numerical difficulties. Haussühl & Siegert (1969) determined for the first time the elastic constants of a triclinic crystal, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$. It is the aim of the present investigation to apply the method used by Haussühl & Siegert (1969) to other crystals in order to test

its applicability and sensitivity. For this purpose we chose ammonium tetroxalate dihydrate (ATO), $\text{NH}_4\text{H}_3(\text{C}_2\text{O}_4)_2 \cdot 2\text{H}_2\text{O}$, and potassium tetroxalate dihydrate (KTO), $\text{KH}_3(\text{C}_2\text{O}_4)_2 \cdot 2\text{H}_2\text{O}$, two isotypical triclinic crystals, which, compared with $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, exhibit a higher optical and elastic anisotropy.

Methods

Sound velocity was measured using the improved Schaefer-Bergmann method (light diffraction by ultrasonic waves in plane-parallel plates). A light beam emerging from a mercury lamp was focused through the crystal (perpendicular to the direction of sound propagation) upon a photographic plate, which was mounted in a distance of about 4 m behind the crystal. Using an ultrasonic frequency of 15 Mc/s it was possible to measure the sound velocity with an accuracy of 0.2%. We made use of the improved method described by Haussühl (1956). In specimens with parallel faces (tolerance, 1μ) standing waves were generated, the frequency being properly adjusted. By variation of the frequency it was usually possible to stimulate and measure each of the three isonormal elastic waves separately and undisturbed. Thus, apart from its higher accuracy, the optical method reveals its superiority over pulse echo methods when applied to transparent compounds. In triclinic crystals, where the three mutually orthogonal displacement vectors are usually inclined with respect to the propagation direction and its normal plane, respectively, all three isonormal waves are generated simultaneously by a longitudinal X-quartz transducer; moreover, they are generated at every reflexion. The consequence on pulse echo experiments is a complex spectrum of superimposed echoes, which can be resolved and analysed only with difficulty.

The single crystals were grown by deposition on seed crystals suspended in saturated aqueous solutions at lowering the temperature from 60 to 30° C. We obtained bright, optically immaculate crystals of about 6 cm in length. According to the IRE-conventions, a

Cartesian coordinate system $\mathbf{e}_1, \mathbf{e}_2, \mathbf{e}_3$ has been chosen as follows:

$$\begin{aligned} \mathbf{e}_2 &\text{ parallel to } \mathbf{a}_2^*; & \mathbf{e}_3 &\text{ parallel to } \mathbf{a}_3; \\ & & \mathbf{e}_1 &\text{ parallel to } [\mathbf{e}_2 \times \mathbf{e}_3] \end{aligned}$$

(\mathbf{a}_i and \mathbf{a}_i^* being the fundamental vectors of the crystal lattice and the reciprocal lattice, respectively, in Groth's (1910) mounting).

From the ATO single crystals seven specimens were cut, the faces of which were naturally grown faces or perpendicular to them. In 15 different nearly homogeneously distributed directions we were able to measure 34 sound velocities. From the KTO single crystals 5 rectangular specimens were cut which were limited by the faces (100), (010), (001), (110), ($\bar{1}\bar{1}0$), (101), (10 $\bar{1}$), (011), (01 $\bar{1}$), (11 $\frac{1}{2}$), ($\bar{1}\bar{1}\frac{1}{2}$), ($\bar{1}\bar{1}\frac{1}{2}$) and (11 $\frac{1}{2}$) (related to the Cartesian system); in these 13 directions 30 different sound velocities were determined. The measurements were carried out at 20°C.

The correlation between the sound velocity, v , measured in a certain direction (direction cosines a_1, a_2, a_3), and the components of the elastic tensor c_{ijkl} is achieved by the following third order determinant (Christoffel's equation):

$$\left| \sum_j c_{ijkl} a_j a_l - \delta_{ik} \rho v^2 \right| = 0 \quad (1)$$

($i, j, k, l = 1, 2, 3$; ρ = density; δ_{ik} = Kronecker symbol).

Each measured value of v , when inserted into (1), yields a third order equation for the 21 unknowns c_{ijkl} . Hence at least 21 measurements are necessary. Additional measurements increase the accuracy. The solution of this redundant non-linear system of equations was obtained by the method of least squares (Haussühl & Siegert, 1969). The c_{ijkl} were fitted in order to minimize the sum of squares of the determinants (1) divided by the derivative of the determinant with respect to ρv^2 .

The method of Marquardt (1963) for the determination of non-linear parameters served as basis for an iteration program. This method produces rapid conver-

Table 1. Elastic stiffnesses c_{mn} ($\times 10^{11}$ dyne.cm $^{-2}$), relative errors $\Delta c_{mn}/c_{mn}$, and elastic compliances s_{mn} ($\times 10^{-12}$ cm 2 .dyne $^{-1}$) of ATO and KTO at 20°C

	mn	11	22	33	12	23	31	44	55	66	14	15
ATO	c_{mn}	2.187	4.589	3.638	1.199	1.629	1.039	1.043	0.540	0.444	0.163	0.599
	$\Delta c/c$	0.6%	0.2%	0.3%	3%	1%	3%	0.9%	2%	2%	10%	2%
	s_{mn}	8.188	4.198	3.517	-1.524	-0.981	-1.296	14.042	27.124	25.447	0.977	-8.069
KTO	c_{mn}	2.536	4.779	3.430	1.184	1.402	0.983	1.019	0.569	0.499	0.072	0.612
	$\Delta c/c$	0.4%	0.3%	0.2%	1%	1%	4%	0.9%	3%	1%	20%	2%
	s_{mn}	6.623	3.740	3.614	-1.021	-0.985	-1.235	14.643	25.926	23.210	0.278	-6.758
	mn	16	24	25	26	34	35	36	45	46	56	
ATO	c_{mn}	-0.103	1.156	0.202	-0.377	0.377	0.203	-0.076	0.014	0.015	0.012	
	$\Delta c/c$	10%	0.7%	10%	2%	2%	5%	30%	80%	60%	80%	
	s_{mn}	0.576	-4.115	0.531	3.167	0.021	0.491	-0.544	0.160	-3.750	-2.088	
KTO	c_{mn}	-0.123	1.134	0.146	-0.270	0.219	0.147	0.040	-0.082	0.053	0.070	
	$\Delta c/c$	8%	1%	10%	3%	5%	5%	50%	10%	10%	10%	
	s_{mn}	2.092	-4.038	-0.477	2.346	0.548	0.890	-1.310	3.215	-4.161	-5.951	

gence by an optimum interpolation between the Taylor series method and the method of steepest descent.

In comparison with a method proposed by Neighbours & Schacher (1967), in which equation (1) is solved with respect to qv^2 , the method we used is thought to exhibit the following advantages: (a) the difficulty of attaching the measured velocities of the quasi-transversal waves to the two derived qv^2 expressions is avoided, (b) the convergence is not in question because of vanishing denominators.

As initial values for the iteration procedure we used for the c_{iiii} the qv^2 values of the fastest waves in the three coordinate axes, and for the c_{ijij} the qv^2 values of one of the slower waves; the remaining c components were put equal to zero.

Results

The results of the calculation are listed in Table 1. Here we made use of the matrix notation for tensor components (Nye, 1957), $m, n=1, 2, 3, 4, 5, 6$ (first row). The second row contains the elastic constants (stiffnesses) c_{mn} in units of 10^{11} dyne.cm⁻², the third row the relative errors as obtained by the least-squares computation. The density ρ used here, was determined by the buoyant force method (in xylene) using specimens free from macroscopic defects, which had a weight of about 15 grams, $\rho_{ATO}=1.653 \pm 0.001$, $\rho_{KTO}=1.858 \pm 0.001$ (the X-ray densities are (Currie, Speakman & Curry, 1967): $\rho_{ATO}=1.654$; $\rho_{KTO}=1.859$ g.cm⁻³). The fourth row of Table 1 contains the components of the tensor of elastic moduli (compliances) s_{mn} , which follow by matrix inversion from $c_{km} \cdot s_{mn} = \delta_{kn}$.

The longitudinal normals, i.e. those directions along which a purely longitudinal wave and two purely transversal waves may propagate, are also the directions of extrema of the longitudinal stiffnesses $c'_{1111} = a_{1i}a_{1j}a_{1k}$

$a_{1i}c_{ijikl}$ (Fedorov, 1968). From a computation of c'_{1111} in different directions we obtained the direction cosines of the longitudinal normals, listed in Table 2(a) together with the appropriate values of c'_{1111} .

The volume compressibility is $K = \sum_{ik} s_{iikk} \cdot K_{ATO} = 8.301 \cdot 10^{-12}$, $K_{KTO} = 7.495 \cdot 10^{-12}$ cm².dyne⁻¹.

According to Haussühl (1967), the deviations from the Cauchy relations may be described by a second-rank tensor g_{rs} :

$$g_{rs} = (c_{iijk} - c_{jikik}) \cdot (-1)^{mn(m-n)/2} \quad (2)$$

($i \neq j; i \neq k; r \neq i, j; s \neq i, k; r, s, i, j, k = 1, 2, 3$). Multiplying by the volume compressibility one obtains a dimensionless tensor $g_{rs}^* = g_{rs} \cdot K$; sign and amount of its components allow conclusions about the form of bonding in the crystal structure. Related to e_1, e_2, e_3 the components of g_{rs}^* are the following:

ATO: $g_{11}^* = 0.486; g_{22}^* = 0.414; g_{33}^* = 0.627$
 $g_{12}^* = 0.075; g_{23}^* = -0.125; g_{31}^* = -0.155$
 KTO: $g_{11}^* = 0.287; g_{22}^* = 0.310; g_{33}^* = 0.513$
 $g_{12}^* = 0.091; g_{23}^* = -0.001; g_{31}^* = -0.002$

Discussion

The values c_{mn} in Table 1 display a graduation as expected: the constants c_{mm} ($m=1, 2, 3$) are 2 to 3 times larger than the c_{mn} ($m, n=1, 2, 3; m \neq n$), and these are larger than the c_{mm} ($m=4, 5, 6$). All the other components are essentially one order of magnitude smaller. Nevertheless, some of them (e.g. c_{24}) are rather large, because the coordinate system e_1, e_2, e_3 , which was chosen rather arbitrarily, has no particular relation to the elastic properties. In orthorhombic crystals, for comparison, the constants under consideration, $c_{mn} =$

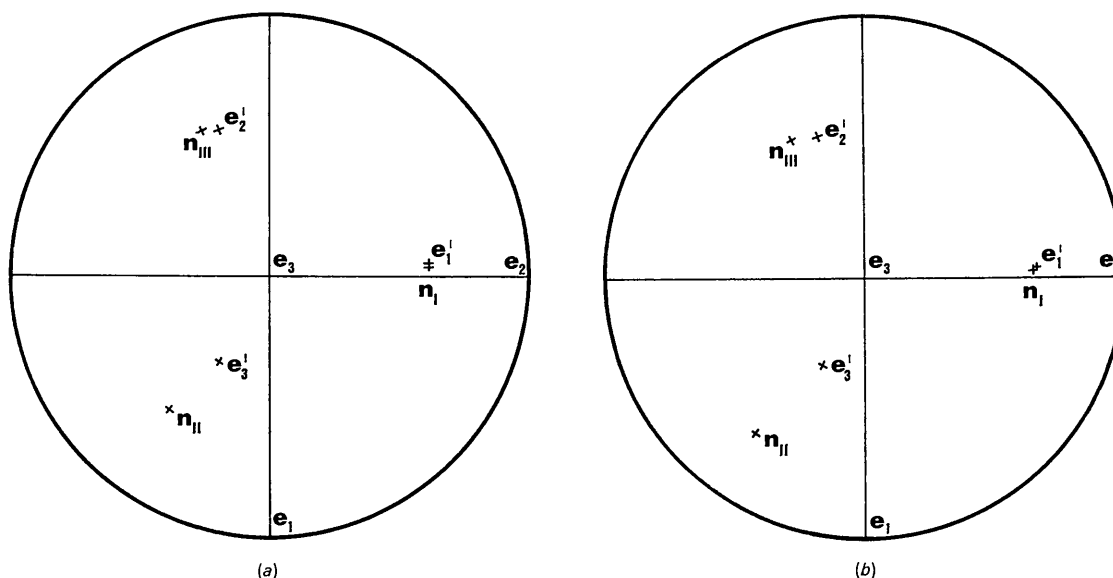


Fig. 1. Stereogram of the longitudinal normals n_i and the axes e'_i belonging to Φ_{min} for (a) ATO, (b) KTO.

c_{rs} ($r=1, 2, 3, 4, 5, 6; s=4, 5, 6; r \leq s$), vanish, if the tensor is referred to the crystallographic axes. If it is referred to other axes, the constants c_{rs} will in general be different from zero. Accordingly, in triclinic crystals a coordinate system e'_1, e'_2, e'_3 should be found, where the constants c_{rs} become as small as possible. A measure of their magnitude is the quantity

$$\Phi = \sqrt{\sum c_{rs}^2}$$

Three particular constants (c_{34}, c_{35} and c_{45}) may be made zero (Fedorov, 1968), when e'_1 is taken along a longitudinal normal and e'_2 and e'_3 along the displacement vectors of the two purely transverse waves propagating along e'_1 . The values of Φ , obtained after the corresponding transformations are (for e'_1 parallel to the maximum (I), saddle point (II), and minimum (III) of c'_{1111} , respectively; units 10^{11} dyne.cm $^{-2}$):

$$\begin{aligned} \Phi_1^{\text{ATO}} &= 0.7063; & \Phi_{\text{II}}^{\text{ATO}} &= 1.003; & \Phi_{\text{III}}^{\text{ATO}} &= 1.086 \\ \Phi_1^{\text{KTO}} &= 0.5591; & \Phi_{\text{II}}^{\text{KTO}} &= 1.117; & \Phi_{\text{III}}^{\text{KTO}} &= 1.121. \end{aligned}$$

The minimal Φ was computed by variation of the Cartesian axes e'_1, e'_2, e'_3 . The direction cosines b_i of these axes, for Φ at minimum, are listed in Table 2(b). The minimal values of Φ are:

$$\Phi_{\text{min}}^{\text{ATO}} = 0.4589 \times 10^{11}; \quad \Phi_{\text{min}}^{\text{KTO}} = 0.3991 \times 10^{11} \text{ dyne.cm}^{-2}.$$

The longitudinal normals n_i and the axes e'_i , for minimal Φ , are shown in a stereogram in Fig. 1. Roughly, these two sets coincide, but it should be noted, that the longitudinal normals n_i are not mutually perpendicular to each other.

The quantity Φ_{min} may be regarded as a measure for the deviation of the elastic behaviour of a triclinic crystal from an orthorhombic crystal and might be called 'triclinicity' (with respect to elasticity). A comparison with other triclinic crystals is possible by means of the dimensionless quantity $T = K \cdot \Phi_{\text{min}}$ (K = volume compressibility).

The only other triclinic crystal measured so far, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, has a triclinicity of about half that of ATO and KTO:

$$T_{\text{ATO}} = 0.381; \quad T_{\text{KTO}} = 0.299; \quad T_{\text{CuSO}_4 \cdot 5\text{H}_2\text{O}} = 0.161.$$

Since the absolute errors of all c_{mn} are in the same order of magnitude, the small constants exhibit a large relative error, as shown in Table 1.

A comparison of the elastic constants of ATO and KTO with other crystals shows, that the elastic anisotropy, which may be defined for instance by the ratio of maximum and minimum of c'_{1111}

$$\left(\frac{c'_{1111}^{\text{max}}}{c'_{1111}^{\text{min}}} \right)_{\text{ATO}} = 4.67; \quad \left(\frac{c'_{1111}^{\text{max}}}{c'_{1111}^{\text{min}}} \right)_{\text{KTO}} = 4.2,$$

is extraordinarily high in the present case (for $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ it is e.g. 1.8). Compared with all crystals previously measured (Bechmann & Hearmon, 1966) this anisotropy is only exceeded by tartaric acid ($c_{11}/c_{22}=4.8$). This strong anisotropy has the consequence, that even a low misorientation of the crystal specimens induces a large change in the sound velocity. This may be the reason that the errors in the present investigation are about the two times those in the $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ measurements. A change of direction by one degree may produce a velocity change of 1.5%. One therefore takes full advantage of the high measuring accuracy of the Schaefer-Bergmann method only, if the accuracy of the orientation of the specimens is guaranteed within 4' (in directions with large gradient).

The deviations of the elastic waves from pure modes are very high, too. The displacement vectors of the quasi-longitudinal waves deviate maximally by an angle of 30° from the propagation direction. Therefore we were able to obtain in almost all directions all three waves by use of a longitudinal quartz transducer.

The principal values of the departures from the Cauchy relations, g_{ii}^* , are positive throughout as usually found in hydrates and crystals with asymmetric constituents (organic molecules) (Haussühl, 1967). Because of the high asymmetry of the NH_4 ion the fact that $g_{ii}^{\text{ATO}} > g_{ii}^{\text{KTO}}$ may also be understood.

Finally we may conclude that the method proposed by Haussühl & Siegert (1969) was successful also in the present case of triclinic crystals possessing high elastic anisotropy, where the initial values for the iteration process differ more strongly from the final values than in more isotropic crystals.

The numerical calculations were carried out with the aid of the IBM 360-75 computer at the KFA Jülich.

We are very much indebted to Prof. S. Haussühl for his kind support in this work.

Table 2. (a) Direction cosines a_i of the longitudinal normals and appropriate value of c'_{1111} ($\times 10^{11}$ dyne.cm $^{-2}$), (b) direction cosines b_i of the coordinate system e'_i belonging to Φ_{min}

	(a)	a_1	a_2	a_3	c'_{1111}	(b)	b_1	b_2	b_3
ATO	Maximum (I)	-0.0466	0.8898	0.4540	5.89	e'_1	-0.0562	0.8896	0.4533
	Saddle point (II)	0.7142	-0.5580	0.4226	2.88	e'_3	0.5649	-0.3461	0.7491
	Minimum (III)	-0.7994	-0.3813	0.4643	1.26	e'_2	-0.8232	-0.2981	0.4831
KTO	Maximum (I)	-0.0400	0.9162	0.3987	5.84	e'_1	-0.0481	0.9179	0.3939
	Saddle point (II)	0.7743	-0.5523	0.3090	3.02	e'_3	0.5814	-0.2950	0.7583
	Minimum (III)	-0.7685	-0.4086	0.4924	1.39	e'_2	-0.8122	-0.2655	0.5195

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Acta Cryst. (1970). **A26**, 405

Thermal Vibrations of Atoms in Ag–Cd and Ag–Zn Solid Solutions

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(Received 14 February 1969 and in revised form 30 May 1969)

From X-ray measurements at room and low temperatures it was found that the characteristic temperature θ of the system Ag–Cd decreases by about 17°K in the concentration range from 0 to 30 at.% Cd. For the system Ag–Zn no systematic change of θ with increasing concentration of Zn was observed.

Introduction

The temperature dependence of the intensity of X-ray Bragg reflexions from solids can be described by the Debye–Waller factor $\exp(-2M)$, which contains the characteristic temperature θ , a parameter characterizing the material.

The present paper describes measurements of the integrated intensity of reflexions from the face-centred cubic metallic solid solutions of cadmium or zinc in silver; these measurements lead to a determination of their characteristic temperature and its dependence on concentration. These alloys are interesting from the following point of view. Measurements of the lattice specific heat and the elastic moduli, C_{ij} , of α -phase alloys of the noble metals near 0°K suggest a change in characteristic temperature θ which is, according to Collins (1967), a function only of the electron/atom ratio for solutions whose ion cores are isoelectronic with the solvent; *i.e.* for the two series of Hume-Rothery alloys for example:

Number of valency electrons

	1	2	3	4	5
Cu:	Zn	Ga	Ge	As	
Ag:	Cd	In	Sn	Sb	

In our case both cadmium and zinc atoms have two valency electrons and hence the valency effect is the

same in both alloys. On the other hand the ion cores of cadmium atoms are identical with the ion cores of silver atoms, whereas the ion cores of zinc atoms are identical with the ion cores of copper atoms. The same valency effects in both systems enable us to determine the influence of the other factors: the different atomic masses of Cd and Zn and the opposing dilatation effects during the substitution into the silver crystal lattice.

Experimental

The measurements were carried out at room and liquid nitrogen temperatures with an URS X-ray diffractometer with the use of monochromatized Cu $K\alpha$ radiation and a Geiger counter.

The samples were cooled in a vacuum chamber* by contact with a copper reservoir filled with liquid nitrogen. The temperature of the sample was determined by means of a thermocouple; the accuracy of the temperature determination was estimated to be about $\pm 4^\circ\text{K}$.

Solid solutions Ag–Cd and Ag–Zn were prepared and homogenized by annealing for about 24 hours in vacuum at a temperature of 650°C according to Birchenal & Cheng (1949). By filing and subsequent grinding a fine powder was obtained. The effects of the deformation of the material were removed by a further anneal for 3 hours in vacuum at a temperature of 500°C. From

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* For a description of this low temperature camera see Valvoda (1969).