Acta Cryst. (1956). 9, 70

The Structure of Rhombohedral *T*(NiCuAl)

By M. G. Bown*

Crystallographic Laboratory, Cavendish Laboratory, Cambridge, England

(*Received* 10 *August* 1955)

Crystals of the ternary compound in the Ni–Cu–Al system have been examined by single-crystal X-ray methods. Two distinct forms were found, one having a rhombohedral, the other a cubic, unit cell. In both forms the heavy and light atoms are arranged as in a CsCl-type structure; ordered vacancies in heavy-atom sites give rise to the two different superlattices. The rhombohedral unit cell contains ideally 8 Al and 6 heavy atoms; in the crystals examined there are also random vacancies in the heavy-atom sites, and possibly in the Al sites. The relationship between the two forms is considered briefly.

1. Introduction

The Ni–Cu–Al system has been investigated by Bradley & Lipson (1938) and by Köster, Zwicker & Moeller (1948). Only one ternary compound was found, with composition field at 500° C. roughly a parallelogram defined by the lines 57·5 and 64 atomic% Al, 5·5 and 10 atomic% Ni. The phase has usually been given the formula $NiCu_3Al_6$: in this paper the letter *T* is used. From powder photographs Bradley & Lipson described the structure as 'distorted body-centred cubic'.

2. Preliminary investigation

Crystals of *T* were kindly supplied by Mr B. Ward of the Metallurgy Department, University of Birmingham, who extracted them electrolytically from slowly-cooled ingots containing *T* and the Al-rich solid solution. They were grey, and of markedly dendritic appearance. Three samples of crystals, extracted from ingots of slightly different initial composition, were made available. Of sample *A* there was insufficient material for a chemical analysis to be made. The analysis of sample *B* was carried out at Birmingham, and gave the composition

$$\text{Ni } 8{\cdot}5,\ \text{Cu } 33{\cdot}4,\ \text{Al } 58{\cdot}1 \text{ atomic\%}\ .$$

Sample *C* was found by Messrs Johnson, Matthey and Company Limited to contain

$$\text{Ni } 6{\cdot}6,\ \text{Cu } 30{\cdot}2,\ \text{Al } 63{\cdot}1 \text{ atomic\%}\ .$$

All the single crystals from sample *A* which were examined showed a cubic unit cell, with $a = 14{\cdot}6$ Å, whereas crystals from *B* and *C* had a rhombohedral unit cell, with $a = 4{\cdot}1$, $c = 40$ Å. By close examination of the single-crystal photographs of *A* and powder photographs of *B* and *C* it was established, however, that both forms were present in all three samples. The two forms are closely related to one another, as will be described later. For convenience, the rhombohedral form will be called T_1 and the cubic form T_2 throughout this paper.

3. Unit cell of T_1

Crystals from sample *B* which gave only reflexions characteristic of T_1, even after very long exposures, were used for further study. Single-crystal photographs showed a hexagonal unit cell, with Laue symmetry $\bar{3}m$. From very high angle reflexions on a van Arkel-mounted oscillation photograph the cell dimensions were found to be

$$a = 4{\cdot}105 \pm 0{\cdot}001,\ c = 39{\cdot}97 \pm 0{\cdot}01 \text{ Å}\ .$$

Systematic absences proved the lattice to be rhombohedral, with possible space groups $R32$, $R3m$ and $R\bar{3}m$. The rhombohedral cell dimensions are

$$a = 13{\cdot}53 \text{ Å},\ \alpha = 17^\circ\ 27';\quad \text{volume} = 194{\cdot}4 \text{ Å}^3.$$

The quantity of crystals in sample *B* was insufficient to make an accurate density measurement by displacement methods, and owing to the high density the flotation method could only set a lower limit of about 4·4 g.cm.^{-3}.

Two of the possible formulae to which the chemical analysis of *B* corresponds are $Ni_{1{\cdot}0}Cu_{4{\cdot}0}Al_7$ and $Ni_{1{\cdot}2}Cu_{4{\cdot}6}Al_8$. The calculated density for one formula unit of the former per rhombohedral cell is 4·3 g.cm.^{-3}, for one of the latter 4·9 g.cm.^{-3}. The composition of T_1 is, of course, not necessarily the same as that of the bulk sample, for T_2 is also present.

4. Structure determination of T_1

Powder photographs showed a close relationship to a body-centred cubic pattern. The cell dimensions are compatible with a structure based on small CsCl-type cubes of side 2·9 Å, for $a = 4{\cdot}1 \risingdotseq 2{\cdot}9\sqrt{2}$, and $c = 40 \risingdotseq 8 \times 2{\cdot}9\sqrt{3}$. This suggests that the large unit cell stretches over eight small cubes along a triad axis of

---

* Now at the Department of Mineralogy and Petrology, Cambridge, England.

the CsCl-type structure, the width being one small cell. On this assumption the rhombohedral cell would contain only a string of alternate heavy and light atoms along the triad axis. Since there must be more Al than heavy atoms in the cell, it is likely that the superlattice is caused by ordered vacant heavy-atom sites, as in Ni_2Al_3.

A photograph of a single crystal rotating about the *c* axis confirmed these ideas, the following features being observed:

(i) On each layer line the intensities of reflexions decreased steadily with increasing angle. This confirms that all the atoms lie on the *z* axis, and on lines related to it by the rhombohedral lattice.

(ii) There were maxima in the intensity distribution at $l = 0, 16, 32$ etc., and smaller maxima at $l = 8, 24$, etc. This would be expected from an arrangement of light and heavy atoms placed alternately at intervals of $c/16$ along the *z* axis. If there were 8 Al atoms along the length of *c*, the composition shows that there would also be about 6 heavy atoms in this length, with two sites vacant.

(iii) The intensities on the remaining layer lines varied roughly sinusoidally with *l*, zeros occurring at $l = 4, 12$, etc.

If the structure contained no ordered vacant sites, these layer lines would not occur. The layers can therefore be considered to be produced by scattering atoms placed in the vacant sites, and only by these atoms. The principle involved is similar to Babinet's principle in optics. Since there are only two vacant sites per cell, a sinusoidal intensity curve would be expected, and from the wavelength of the observed curve it can be deduced that the vacancies are separated by $c/8$.

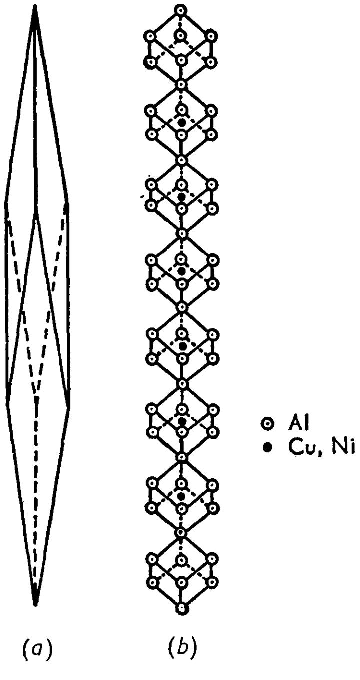

Fig. 1. Unit cell of T_1. (*a*) Outline of rhombohedral cell. (*b*) Illustration of how the structure is built up from small cubes, with two vacant sites.

The idealized structure is illustrated in Fig. 1. Intensities calculated from this model agree moderately well with observations.

5. Refinement of structure

Zero-layer Weissenberg photographs were taken with filtered Mo radiation about the *a* and a^* axes of the hexagonal cell, recording $h0\bar{h}l$ and $h,h,\overline{2h},l$ reflexions respectively. The multiple-film technique was used, and the 80 observed non-zero intensities were estimated visually. The crystal used had cross-section $0{\cdot}05 \times 0{\cdot}09$ mm^2: for Mo $K\alpha$ radiation $1/\mu = 0{\cdot}06$ mm. The intensities were corrected for absorption by the graphical method of Joel, Vera & Garaycochea (1953), and for Lorentz and polarization factors.

The exact *z* parameters of the atoms can be found by a one-dimensional Fourier projection on to the *z* axis. If the normal method of projection is used the repeat distance is $c/3 = 13{\cdot}3$ Å, owing to the rhombohedral symmetry; this leads to a peak separation of 0·83 Å, which is rather small for accurate work. $000l$ reflexions, which occur with $l = 3n$ only, would be used for this projection. A method was found for increasing the repeat distance to the full 40 Å without using complete three-dimensional data. In planes normal to *z* the only variation in the Fourier transform of the scattering unit (which is the row of 14 atoms along *c*) is due to angular decrease of scattering factors. The observed reflexions allow this transform to be sampled at certain points on an equally spaced set of such planes, $l = 0, 1, 2, \ldots$, etc. By extrapolation for each layer the values of $|F(000l)|$ can be found for *all* *l*, although only those having $l = 3n$ are directly observable. Inversion of the transform by a one-dimensional Fourier series using these values would give a projection of the scattering unit on to the *z* axis, with the full repeat distance of 40 Å.

An analytical method of extrapolation was used, each $|F(hkil)|$ being divided by $\hat{f}$, a mean unitary scattering factor, and by a temperature factor $t = \exp(-B\sin^2\theta/\lambda^2)$. The best value of *B*, found from the mean slope of graphs (for each layer) of $\log(|F|/\hat{f})$ against $\sin^2\theta/\lambda^2$, was $0{\cdot}55 \times 10^{-16}$ Å^2. For each layer $|F|/\hat{f}t$ should be constant, and values were found to have a standard deviation of about 5% from the average. Using the appropriate $\hat{f}$ and *t*, $|F(000l)|$ was found for all *l*; the resulting values should be more accurate than if they had been directly observed.

The length of the *c* axis made it necessary to evaluate the Fourier summations at $1\frac{1}{2}°$ intervals. An F_o synthesis, calculated on the assumption of a centrosymmetric structure, is shown in Fig. 2(*a*). The decrease in peak heights near the origin was proved, by comparison with corresponding F_c syntheses, to be mainly due to the omission of reflexions too weak to be observed. This effect has been eliminated in the refinement by the use of difference syntheses.

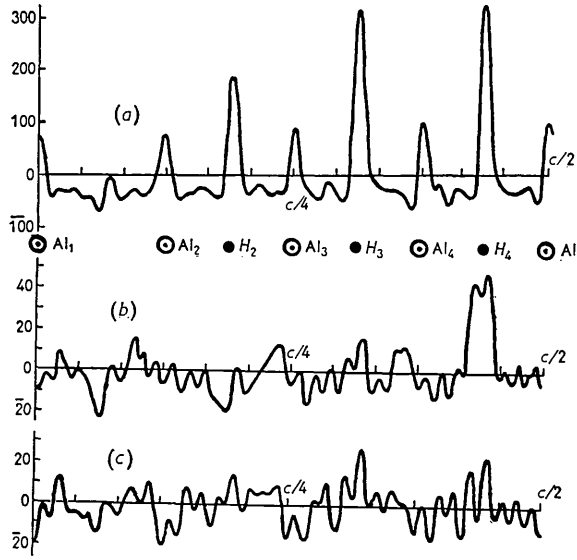

Fig. 2. Fourier projections of T_1 on [0001]: (a) F_o synthesis; (b) ($F_o - F_c$) synthesis, assuming complete occupation of all (occupied) sites; (c) ($F_o - F_c$) synthesis, assuming deficiencies in H_3 of 15%, in H_2 of 32%, and in all Al sites of 12·5%.

It has been assumed that the structure is centrosymmetric. If this were not so, the peaks in the F_o synthesis would be broadened, and in a difference synthesis there would be a negative region at the atomic position, flanked by two positive regions; no effects of this kind were found. The final difference synthesis, calculated for complete occupation of all sites (except the vacant ones) is shown in Fig. 2(*b*). The agreement index, R, is 0·14. The peak at H_4 is little affected by parameter changes, but it can be reduced by assuming that other sites are only partially occupied. With 7% deficiency in H_3 and 14% in H_2, (equivalent to a formula unit $Ni_{1.2}Cu_{4.6}Al_8$ per cell) the peak at H_4 was reduced by about one-third and R fell to 0·12. With 15% deficiency in H_3, 32% in H_2 and 12·5% in each Al site, Fig. 2(*c*) was obtained, and $R = 0{\cdot}10$. This model has a formula unit $NiCu_4Al_7$ per rhombohedral cell; it gives a better difference synthesis than can be obtained if the Al sites are taken to be fully occupied.

The effect of deficiencies in the f curves used in calculating F_c (see Black, 1955) has been considered, but makes no substantial difference in this case. Indicated parameter changes are markedly dependent on the occupation of sites: refinement could be continued on an assumed model, but without reliable density and composition measurements there is little justification for this procedure.

Table 1. *z parameters*

Site	Ideal	Final	Shift (Å)
Al_1	0	0	0
Al_2	±0·1250	±0·1255	0·02
Al_3	±0·2500	±0·2515	0·06
Al_4	±0·3750	±0·3800	0·20
Al_5	0·5000	0·5000	0
H_2	±0·1875	±0·1900	0·10
H_3	±0·3125	±0·3145	0·08
H_4	±0·4375	±0·4380	0·02

Sites H_2, H_3 and H_4 are occupied by Cu or Ni atoms. Standard deviation of parameters (about) 0·001.

Table 2

l	$\lvert F(000l)\rvert$ deduced	$\lvert F(000l)\rvert$ calculated (a)	(b)	(c)
0	84	84	84	84
1	22	16	18	20
2	9	12	9	7
6	7	10	8	6
7	16	13	15	17
8	23	21	18	19
9	23	16	17	19
10	9	12	10	8
14	10	12	11	9
15	10	3	5	7
16	56	58	58	58
17	23	20	20	22
23	8	7	9	11
24	15	13	12	13
25	18	13	14	15
26	6	8	8	6
30	7	8	7	6
32	36	36	36	36
33	19	17	17	18
40	8	9	9	8
41	13	12	12	13
42	6	5	4	4
48	19	21	22	22
49	14	23	13	14
57	7	9	9	10
64	7	11	11	12
65	7	9	9	10

For l values not included in this table no reflexions were observed, and the calculated $\lvert F\rvert$ values are all $\leqslant 6$. F_c has been scaled to F_o. Column (*a*) was calculated for a model assuming complete occupation of all sites; column (*b*) for H_3 7% deficient, H_2 14% deficient; and column (*c*) for H_3 15% deficient, H_2 32% deficient, and all Al sites 12·5% deficient.

Final parameters are given in Table 1. Table 2 contains values of $\lvert F(000l)\rvert$ deduced from observations and calculated for each of the three models mentioned above. Complete lists of F_o's and interatomic distances are available in a thesis (Bown, 1955). It was not possible to distinguish between Cu and Ni atoms on the basis of interatomic distances. The (Cu, Ni)–Al distances all lie between 2·46 and 2·62 Å, with the sole exception of the H_4–Al_4 distance of 2·32 Å. This seems to be significantly less than the mean (2·52 Å) but the reason is not understood. The mean distance agrees well with values found in the similar structures NiAl and Ni_2Al_3 (Bradley & Taylor, 1937) when allowance is made for the fact that the radius of Cu is about 0·03 Å greater than that of Ni. Thus in NiAl, Ni–Al = 2·50 Å, and in Ni_2Al_3, Ni–Al =

2·43–2·52 Å (mean value 2·47 Å). The mean values, with the range of values in brackets, of the other interatomic distances in T_1 are: Al–Al, 2·90 (2·76–3·02 Å); (Cu, Ni)–(Cu, Ni), 2·87 (2·79–3·02 Å). These are also in agreement with the comparable distances in NiAl and Ni_2Al_3.

6. The cubic form, T_2

The crystals from sample *A* had a cubic unit cell of side $a = 14·6$ Å, and Laue symmetry *m*3*m* (certainly to a close approximation). The following rules governed the appearance of reflexions:

h, k, l all $= 5n$	
$h+k+l = 10n$	very strong
$h+k+l = 10n+5$	strong
h, k, l all $= 5n\pm2$	medium strength
h, k, l all $= 5n\pm1$	weak

(n = any integer; h, k, l not necessarily all equal). No other reflexions due to T_2 were observed.

This structure is also based on CsCl-type cubes, there being 125 in the large cell. The superlattice is caused by ordered vacancies, and an arrangement of these was found which would account qualitatively for the observed reflexion rules. No truly single crystal of T_2 was found, so that no accurate intensity measurements could be made. The proposed structure is not reported here, since quantitative confirmation has not yet been obtained, but details are available in a thesis (Bown, 1955).

The pattern of reflexions given by T_2 is very nearly identical with that which would be given by a four-component multiple twin of the rhombohedral form, with the four triad axes parallel to the triads of a cube. Positions and intensities of corresponding spots would be very similar. No twinning of T_1 has been observed, however.

All the crystals of the cubic form examined gave streaks on single-crystal photographs running from the cubic towards the rhombohedral spot positions, and some of these streaks ended in spots in the rhombohedral positions. It is suggested that the cubic form is metastable at room temperature, and has partially transformed into the rhombohedral form during the slow cooling of the ingot.

A further investigation of the relation between the two forms is to be made.

7. Discussion

The ideal structure of T_1 has two vacant sites per cell, giving a formula $(NiCu)_6Al_8$. The crystals examined show partial occupancy of other heavy-atom sites, and there is some evidence for supposing that only about 7 Al atoms are distributed over the 8 Al sites.

The structure of T_1 has been determined as part of a programme of research aimed at discovering the important factors in the formation of Al-rich alloys containing transition metal atoms. One of these factors is thought to be the electron concentration; T_1 and similar structures are now considered from this point of view.

In the β-phase (NiAl) of the Ni–Cu–Al system it has been established by Lipson & Taylor (1939) that random vacancies first appear in heavy-atom sites at 3·0 electrons/cube. At this electron concentration the surface of the distribution just touches the planes of the first Brillouin Zone. However, despite an increasing number of vacancies, the electron concentration rises to 3·4 at the Cu-rich corner of the phase field, if Ni is zero-valent. The concentration can be kept at 3·0 electrons/cube if the Ni atoms are assumed to have a variable negative valency up to a maximum of 0·8. The same is true for the corresponding phase in the Fe–Cu–Al system, the maximum negative valency of Fe necessary being 2·8. These maximum negative valencies are similar to the values, 0·61 and 2·66, proposed by Raynor (1944) for Ni and Fe respectively, to correlate experimental results on Al-rich alloys containing transition metals.

In Ni_2Al_3, also based on CsCl-type cubes, there are again 3·0 electrons/cube. The effect on the electron concentration of the solution of Cu in this phase has not been investigated.

In the T_1 phase, if there are 8 Al atoms per cell, the negative valency of Ni needed to make the electron concentration 3·0 electrons/cube is 3·8, but if there are only 7 Al atoms per cell a negative valency of 0·6 for Ni brings the figure to 3·0. This fact, considered in relation to the cases of β(NiAl) and Ni_2Al_3, is at least suggestive, though the real significance of these assumed negative valencies remains obscure. Moreover, it must not be forgotten that the present structural investigation, though strongly suggesting unit-cell contents of $NiCu_4Al_7$, is not regarded as proving conclusively that this is the case.

The relation between the structures of Ni_2Al_3 (Bradley & Taylor, 1937) and T_1 can be expressed in terms of the planes of heavy-atom sites perpendicular to the triad. In Ni_2Al_3 one in three of these planes is devoid of atoms, the sequence being

$$\ldots, XOX, XOX, \ldots \text{ etc.},$$

where X denotes an occupied plane and O an unoccupied one. In the same notation the ideal structure of T_1 is

$$\ldots OX, XOXXXXOX, XO \ldots \text{ etc.}$$

Köster & Moeller (1941) discovered a phase in the Cu–Zn–Al system which gave the same powder pattern as T. The limits of composition of this phase at 500° C. can be written, approximately, Cu_5ZnAl_7 and $Cu_{6.4}Zn_{2.5}Al_{6.5}$, which suggests that the Zn atoms are in the Al sites, as might be expected from the metallic radii.

I wish to thank Prof. G. V. Raynor and Mr B. Ward for providing the specimens. I am indebted to Prof. Sir Lawrence Bragg, Prof. N. F. Mott and Dr W. H.

Taylor for provision of facilities and for their interest in the progress of this work. I have to thank the Department of Scientific and Industrial Research for financial support.

References

Black, P. J. (1955). *Phil. Mag.* (7), **46**, 155.

Bown, M. G. (1955). Ph.D. Dissertation, University of Cambridge.

Bradley, A. J. & Lipson, H. (1938). *Proc. Roy. Soc.* A, **167**, 421.

Bradley, A. J. & Taylor, A. (1937). *Phil. Mag.* (7), **23**, 1049.

Joel, N., Vera, R. & Garaycochea, I. (1953). *Acta Cryst.* **6**, 465.

Köster, W. & Moeller, K. (1941). *Z. Metallk.* **33**, 278.

Köster, W., Zwicker, U. & Moeller, K. (1948). *Z. Metallk.* **39**, 225.

Lipson, H. & Taylor, A. (1939). *Proc. Roy. Soc.* A, **173**, 232.

Raynor, G. V. (1944). *J. Inst. Met.* **70**, 531.

Acta Cryst. (1956). **9**, 74

Kristallgittermodelle infolge von elektrischer Aufladung bei Kristallisation

Von Brigitte Krause und M. Renninger

Kristallographisches Institut der Universität, Marburg-Lahn, Deutschland

(*Eingegangen am* 25. *April* 1955)

Small crystals of pentaerythritol crystallizing from aqueous solution and floating on the surface, if of uniform size, are found forming a regular hexagonal array. This is shown to be caused by the interaction of the capillary attraction and the electrostatic repulsion of negative charges on the growing crystals. The sign of the charge reverses if the crystals, after a period of growth, dissolve again. The potentials to which the crystals are charged can reach several hundred volts and are proportional to the length of the crystal edges. Details of the arrangement can be explained quantitatively by a relation between the edge-lengths of two interacting crystals and their distance. It is surmised, but could not be proved, that the interaction is due to unipolar charges 'frozen in' all over the volume rather than to a double layer located at the surface of the crystals. The possible relation of the effect to Ribeiro's thermo-dielectric effect is pointed out.

1. Allgemeine Beobachtungen

Nachfolgend wird berichtet über Bemühungen um Aufklärung einer vor einigen Jahren bei Kristallisationsversuchen mit Pentaerythrit gemachten Beobachtung: Die an der Oberfläche einer warmgesättigten wässerigen Pentaerythrit-Lösung nach Kristallisationsbeginn (durch Abkühlung) schwimmenden Kristallkeime ordnen sich, sofern sie einheitliche Grösse haben, regelmässig an zu einer Art von zweidimensionalem Gitter, einer hexagonalen 'dichtesten Kreispackung' ähnlich derjenigen der Seifenbläschen im Bragg–Nye'schen Modell (1947*a*, *b*).

Fig. 1 zeigt die Erscheinung in zwei Mikroaufnahmen.* Man erkennt, dass die hexagonale Symmetrie sich nur auf die Anordnung der Kriställchen, nicht aber auf deren Form erstreckt. Der Querschnitt der Kristalle ist nämlich quadratisch entsprechend der tetragonalen Struktur von Pentaerythrit. Sie schwimmen mit vertikaler c-Achse und bilden quadratische Bipyramiden (Fig. 2(*a*)) mit (101)-Flächen der raumzentrierten tetragonalen Zelle (und damit Oktaederflächen der pseudokubisch flächenzentrierten Zelle) gegen das Lösungsinnere und ($10l$)-Flächen gegen den Luftraum. Dabei ist $l \gg 1$. Manchmal wachsen die Kristalle säulenförmig weiter ins Lösungsinnere und erscheinen dann wie aus parallelverwachsenen Einzelkristallen aufgebaut (Fig. 2(*b*)). Ihre Projektion auf die Lösungsoberfläche jedenfalls hat immer nahezu quadratische Form, und die Kanten dieser Quadrate bilden regellos verteilte Winkel mit den drei hexagonalen Hauptrichtungen der Anordnung.

Diese Beziehungen gelten nur so lange, als der Abstand zwischen Nachbarkristallen ein Mehrfaches der Kristallgrösse beträgt. Bei Kleinerwerden des Verhältnisses zwischen beiden tendieren die Kristalle zu Parallelstellung ihrer Kanten (Fig. 1(*c*)). Dadurch wird eine der drei vorher gleichberechtigten Richtungen ausgezeichnet und die hexagonale Symmetrie der Anordnung in eine rhombische übergeführt. Die Grenze zwischen beiden Gitter-Arten liegt bei einem Verhältnis Abstand/Grösse von etwa 3–4.

---

* Die Mikroaufnahmen wurden hergestellt mit Hilfe einer von der Firma Ernst Leitz Wetzlar (Herrn W. Freund) freundlichst zur Verfügung gestellten mikrophotographischen Einrichtung geringster Vergrösserung (3-fach auf Kleinbildformat), bestehend aus einem Mikroskop-Stativ älterer Bauart, das die Verwendung des heute nicht mehr gefertigten Objektivs Nr. 0 ermöglicht, dazu einem Photoaufsatz mit Leica. Der kleine Abbildungsmasstab entsprach dem Wunsch nach einem möglichst grossen Bildfeld bei noch ausreichend guter Erkennbarkeit der einzelnen Kristallformen.