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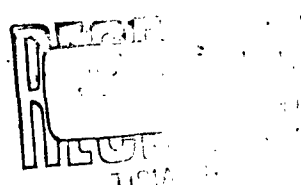
Written Discussion by:

Henry M. Otte

X-ray Diffractometer Determination of the Thermal Expansion
Coefficient of Aluminum Near Room Temperature

H. M. Otte, W. G. Montague and D. O. Welch

June, 1963



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Written Discussion

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Ordered Clusters.

A "compromise" between interpretations in terms of clustering and in terms of SRO as presented by Clarebrough, Hargreaves and Loretto⁽¹⁾ would be an interpretation in terms of clusters with a high degree of order. Such an interpretation has been proposed⁽²⁾ and also its "converse", namely that disordering and ordering proceed by the growth and dissolution of disordered clusters⁽³⁾. In a careful analysis of the X-ray diffuse scattering from Cu-16 at.%Al Borie and Sparks⁽⁴⁾ determined that a short-range structure of the alloy consistent with the data was one in which the Al atoms were situated on the FCC lattice in such a way that a group of 4 Al atoms would be next-nearest neighbors and would form a tetrahedron. This is illustrated in Fig. 1; the arrangement requires local composition increases to (or clusters containing) 18.75 to 25 at.%Al. Clusters of such tetrahedra are assumed to be randomly oriented (relative to each other) and distributed throughout the crystal, their density in the alloy being determined by its composition. Specific heat measurements quoted by Wechsler and Kernohan⁽⁵⁾ for a Cu-16.8 at.%Al

alloy show that the energy associated with the changes in this alloy around 200-300°C are the same order of magnitude as found for Cu-Zn by C-H-L⁽¹⁾.

In connection with the interpretation of a decrease in lattice parameter, a_0 , as being due to SRO, the results we obtained on a Ag-25Zn alloy (prepared by Kittl and Massalski) may be of interest. Addition of Zn decreases a_0 of Ag, whereas it increases a_0 of Cu. If we therefore assume the α -phases of CuZn and AgZn to be sufficiently similar in that SRO produces a decrease of a_0 in both cases, then in AgZn it becomes possible in principle to distinguish between SRO and clustering.

Table I gives the results obtained for filings and for a solid rod, aged 1008 hrs. at 120°C of the Ag-25Zn alloy. Whereas the filings show no change in a_0 , the solid rod shows an increase of about 0.0005 Å (corresponding to a loss of 0.27%Zn from the matrix). Ageing cold-worked filings for 1008 hrs. at 120°C showed no significant change in a_0 either, although a small decrease in the stacking fault probability (from $\alpha = 0.021$ to $\alpha = 0.017$) was apparent, as judged by the change in displacement of the peaks, especially the 111, 200 peaks.

The atomic mobility around 100°C in the Ag-25Zn alloy is about 500 times greater than in Cu-30Zn alloy^(6,7,8), so that one could attribute the lack of a change in the filings (Table I) to the fact that a stable configuration had probably been attained in the alloy after quenching and during the period that the filings were compacted and allowed to dry prior to the X-ray measurement. A similar explanation would apply to the observations on the cold-worked filings. In the solid, on the other hand, one could suppose

that after quenching, an insufficient concentration of vacancies was retained to permit rapid approach to a more stable configuration (ordered clusters). In contrast to these observations, C-H-L⁽⁸⁾ found that in 0.5 mm (0.020 in) diameter wires of Ag-27Zn no change occurred in the resistivity up to 150°C (on heating at 2°C/min.) after slow cooling, but if instead the alloy was quenched from 600°C then, upon heating at the same rate, the resistivity first decreased up to 70°C and then increased. However, the experimental conditions are sufficiently different from those used by us, and the data relatively few in both cases, so that a strict comparison is probably not warranted.

According to the data of F-N-R⁽⁷⁾ for 75-25 and 70-30 brass, one would expect the reaction kinetics for 63-37 brass to be extremely rapid at 240°C (i.e. completed within 1 hour) whereas Massalski and Kittl's work⁽⁹⁾ shows that on the contrary many days are required. This as well as Thomas' observations⁽¹⁰⁾ that furnace cooled or aged Cu-(30-34)Zn alloys have a higher stacking fault energy by a factor of up to 2, than the quenched alloys, point to significant differences that exist in the behavior at low temperatures (<300°C) of α -brass with composition near the phase boundary (i.e. >30%Zn) and that of α -brass with 30%Zn or less.

Acknowledgement

I would like to acknowledge the Office of Naval Research for financial support.

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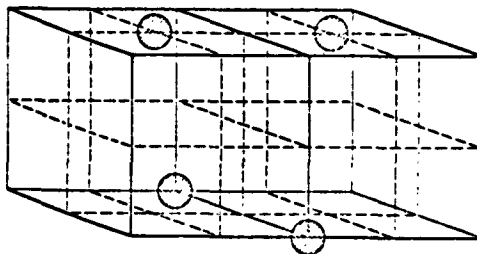


Fig. 1. Two Face-Centered Cubic Unit Cells Showing the Proposed Distorted Tetrahedral Aluminum Array. The face centers are marked by intersections of the dashed lines. Other atomic sites in the vicinity of the four aluminum atoms are presumed to be occupied by copper.

(By courtesy of Borie and Sparks.)

Table I
Effect of Aging a Ag-25Zn Alloy at 120°C.

Specimen Condition	Treatment	α_0 in A°(at $24 \pm 1^\circ\text{C}$)*
Fillers compacted into rods 2.2 mm dia. after treatment.	1 hr. at 700°C, WQ	4.0401 $\pm$ 1
	1 hr. at 700°C, WQ	
	+ 1008 hrs. at 120°C	4.0401 $\pm$ 1
Solid Rod 2.95 mm dia.	1 hr. at 700°C, WQ	4.0393 $\pm$ 1
	1 hr. at 700°C, WQ	
	+ 1008 hrs. at 120°	4.0398 $\pm$ 1

* extrapolated value.

X-ray Diffractometer Determination of the Thermal Expansion
Coefficient of Aluminum Near Room Temperature

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In order to test the precision in the lattice parameter measurement attainable on the X-ray diffractometer with the D(ebye)-S(cherrer) arrangement⁽¹⁾, the coefficient of thermal expansion of aluminum was measured over a small temperature range near room temperature. The results obtained indicated that a precision of $5:10^7$ was possible when comparing extrapolated values of the lattice parameter, a_0 . This is an order of magnitude better than is possible from the measurement of only one diffraction peak in the back reflection region (e.g. refs. 2, 3, and 4) except when using elaborate procedures⁽⁵⁾ compared with the above⁽¹⁾.

The project was initiated as a consequence of results presented in an earlier paper⁽¹⁾, in which values of a_0 for aluminum were found to be reproducible to within $\pm 0.00005 \text{ \AA}$ when the RT (24°C) was maintained constant to $\pm 1^\circ\text{C}$. Straumanis⁽⁶⁾ has pointed out that these data appear to be inconsistent. From the value for the coefficient of thermal expansion of aluminum (Fig. 1) it is easily calculated that a variation of $\pm 1^\circ\text{C}$ corresponds to almost $\pm 0.0001 \text{ \AA}$ variation in a_0 . Two possible explanations exist: (1) the temperature fluctuations of the specimen were less than the RT fluctuations and (2) the extrapolation method tends to suppress the effect of the temperature fluctuations. Both explanations were in fact found to be valid⁽¹⁸⁾ and to enhance the reproducibility

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of a_0 .

As a more sensitive test of the effect of temperature fluctuations, a_0 was measured over a small temperature range to determine the coefficient of thermal expansion. Apart from details given here, all other details were the same as in reference 1.

Unlike in the case of the standard diffraction method with flat samples, in which the temperature can be easily controlled by a heater or cooling coils behind the sample, in the D-S method on the diffractometer, this is not possible, since the cylindrical sample is spinning. Instead, the temperature of the surrounding air must be changed. Measurements were made at 19°, 24° and 29°C by changing the temperature of the room, and also by changing the temperature around the specimen only and maintaining the room temperature at $24 \pm 1^\circ\text{C}$. The former method did not give satisfactory or reproducible results (even after several modifications to the air circulation system). There were too many possible causes for this to check them all out. The latter method, used by Straumanis⁽¹⁷⁾ in his film camera and by others, proved satisfactory and was used to obtain a_0 also at 39°C. The temperature cycles were recorded at the same time as the line profiles; the exact shape and duration of a cycle depended mainly on the temperature being maintained. The maximum temperature variation is given in Table I together with the results obtained for a_0 . For the 29°C run the temperature control was (unintentionally) poorer than in the other three runs, for which $\pm 0.5^\circ\text{C}$ is a conservative estimate. The temperature change during the scanning of most profiles was generally appreciably less. Excluding the 29°C value, we obtain for the coefficient of thermal expansion $\alpha = 23.4 \times 10^{-6}$ for

aluminum (with an estimated error of $\pm 0.2 \times 10^{-6}$). This is in good agreement with the data in the literature^(3,4,7-14), as Fig. 1 shows. In order to detect the small increase of about 0.3×10^{-6} in α in going from 19 to 39°C, the precision of the measurements would have to be increased by a factor of about 5, i.e. to $1:10^7$. For the temperature range 19-39°C, the data of Nix and McNair⁽⁷⁾ give an average $\alpha = 24.5 \times 10^{-6}$ with a great deal of scatter due to making measurements at smaller temperature intervals (1.0 to 4.0°C) than warranted. Straumanis and Cheng⁽⁴⁾ obtained $\alpha = 22.8 \times 10^{-6}$ in the range 10° to 60°C for a hard wire whereas for a powder Straumanis⁽⁸⁾ reported 23.31×10^{-6} . The mean value of a_0 (excluding that from the 29°C measurement) is $4.0492 \text{ } 46 \pm 2 \text{ } \text{\AA}$, corresponding to an "effective" temperature fluctuation of $\pm 0.02^\circ\text{C}$, and agrees well with $a_0 = 4.04925 \pm 05 \text{ } \text{\AA}$ published earlier⁽¹⁾, in which a precision commensurate with the accuracy was used. The value is perhaps a fraction on the low side compared with most other measurements⁽⁵⁾, and this could be due to the use of a monochromator⁽¹⁵⁾. However, though different settings of the monochromator affected the intensities, little effect could be detected on the line position averaged from readings on both sides of the beam.

In reference 1 it was inadvertently stated (footnote 20, ref. 1) that Straumanis did not report the temperature at which he made certain measurements of a_0 for aluminum⁽¹⁶⁾; they were, as a matter of fact, actually quoted in his Fig. 4⁽¹⁶⁾. His a_0 values after correcting for temperature are reproduced in Table II and are the same from planes parallel and perpendicular to the wire axis, so that Straumanis' statement in his paper⁽¹⁶⁾ (page 1967)

that "There is a difference in the a_0 constants of aluminum in two perpendicular directions of the wire, which decreases only slightly if temperature corrections were made" is incorrect on the basis of the data in his Figure 4⁽¹⁶⁾, but seems to be verified by his work with Cheng⁽⁴⁾, as Table II shows. The apparently contradictory results of Straumanis and of Straumanis and Cheng may be a consequence of making measurements on specimens with a different geometry (discs instead of wires) so that new sources of error are introduced and the accuracy of measurement is actually lower than claimed. The size of the discs was essentially the same in both investigations: a main source of error could arise from the difficulty in aligning very small discs sufficiently accurately. However, Otte's conclusion⁽¹⁾, that a_0 (measured from planes parallel to the wire axis) is the same for annealed and for cold-drawn wires is verified by Straumanis and Cheng (Table II). The absence of any effect may be due to the rapid recovery at RT of high purity aluminum.

Thus although the precision in Straumanis' measurements may under certain conditions be quite high, his accuracy is probably no higher than in the present diffractometer technique, which has the added advantage of being able to measure the lattice parameter from the broad diffraction lines of heavily cold-worked metals. Improvement in the precision (but probably not the accuracy) of the diffractometer technique can be easily obtained by a closer temperature control, and this has been demonstrated by measuring the coefficient, α , of thermal expansion of aluminum over a temperature range of only 20°C. The result: $\alpha(19-39^\circ\text{C}) = 23.4(+0.2) \times 10^{-6}$.

Acknowledgement

We would like to thank the Office of Naval Research for financial support.

Caption

Fig. 1. Linear thermal expansion coefficient, α , of aluminum as a function of temperature. Present result (~~xxx~~) compared with data from the literature: S(—) ref. 8; N-M (Δ) ref. 7; R($\Diamond$) ref. 10; W($\times$) ref. 9; H-S($\square$) ref. 12; H-K ($\boxplus$) ref. 13; F-J-R(∇) ref. 14; S-B($\circ$) ref. 3; S-C(---) ref. 4. The data of N-M have been averaged over 20°C intervals.

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- 18) Temperature fluctuations were measured with a thermistor to a precision of $\pm 0.5^\circ\text{C}$. The cooling cycle lasted 6 ± 1 min. and the warming cycle 13 ± 2 min., such that the time for one cycle was always 19 ± 2 min. The temperature was controlled by a wall thermostat placed a few feet from the specimen. The thermistor readings indicated that the RT fluctuated by $\pm 0.95^\circ\text{C}$ whereas the specimen temperature fluctuated only by $\pm 0.70^\circ\text{C}$. The diffraction line for a given reflection was always recorded from high to low angle on one side of the beam and v.v. on the other side; since the duration of the warming and cooling cycle were not the same, the effect of the temperature fluctuations on the line profile was not "symmetrical". This, together with the fact that the line profiles were recorded at random with respect to the temperature cycles made the extrapolated a_0

values less sensitive to temperature fluctuations than one would at first expect. When the length of a complete temperature cycle is of the same order of magnitude as the time required to record a peak, then the precise shape and position of the line profile is measurably dependent on the point in the temperature cycle at which the recording of the profile is commenced. However, if the peak positions are estimated only to $\pm 0.005^\circ 2\theta$, then the effect is a borderline issue: thus test runs indicated that the center of gravity of the diffraction line was never displaced by more than $0.005^\circ 2\theta$ (though the peak position tended to be affected more strongly) even in the high angle region where it took one temperature cycle to record the profile.

TABLE I

Extrapolated lattice parameter a_0 (in Å) for 99.99% Aluminum polycrystalline rod 3.12 mm diameter. $\text{CuK}\alpha_1$ radiation ($\lambda = 1.54050(0)\text{Å}$).

Temp. of measurement $t^\circ\text{C}$ (max. $\pm$)	$a_0(t)$	$a_0(24^\circ\text{C})$ for $\alpha = 23.4 \times 10^{-6}$
19.3($\pm$ 0.5)*	4.0488 00	4.0492 46
24.2($\pm$ 0.5)*	4.0492 64	4.0492 45
29.3($\pm$ 0.8)	4.0497 65	4.0492 62
39.2($\pm$ 0.5)*	4.0506 94	4.0492 48

Room temperature $24 \pm 1^\circ\text{C}$. Curved quartz crystal monochromator. Scanning rate: 10 min. per deg. 2θ . Sample spinner: 150 rpm. Values of a_0 obtained using the Nelson-Riley or Taylor-Sinclair function and linear extrapolation from a least squares fit with weighting factor $\tan\theta$. Specimen not removed from diffractometer while temperature changed.

* "Effective" temperature fluctuations (see text), $\pm 0.02^\circ\text{C}$.

TABLE II

Lattice Parameter (a_0) of Al.

Values of a_0 in Å corrected to 24°C

The number in parentheses after a_0 gives the number of measurements made.

Investigator	Annealed Wire	Cold Drawn Wire	
	(Wire Axis)	Wire Axis	⊥ Wire Axis
Straumanis (1959)	-----	4.0493 (1)	4.0493 (1) [†]
Straumanis and Cheng (1960)	4.0493 ₈ (2?) (s=+0 ₄ ; Δ?)	4.0493 ₅ (6*) (s=+0 ₃ ; Δ=+0 ₄ , -0 ₇ max.)	4.0495 ₄ (6*) ^{††} (s=+0 ₄ ; Δ=+0 ₈ , -0 ₇ max.)
Otte (1961)	4.0492 ₅ (1)	4.0492 ₅ (6) (Δ=+0 ₅ maximum)	-----

† size of disc used in measurement: 0.12 mm x 0.28 mm dia.

†† size of disc used in measurement: 0.12 mm x 0.25 mm dia.

- * Average of 6 different measurements (each the average of at least two measurements) at 6 different temperatures (10, 20, 30, 40, 50 and 60°C), then corrected to the same temperature, and the "most probable error" or, standard deviation (given in brackets) calculated from $s=+0.675 \sqrt{\sum \Delta^2 / (n-1)}$, where Δ = maximum deviations from average value, and n = number of measurements; s=+0₃ means s=+0.0000₃.

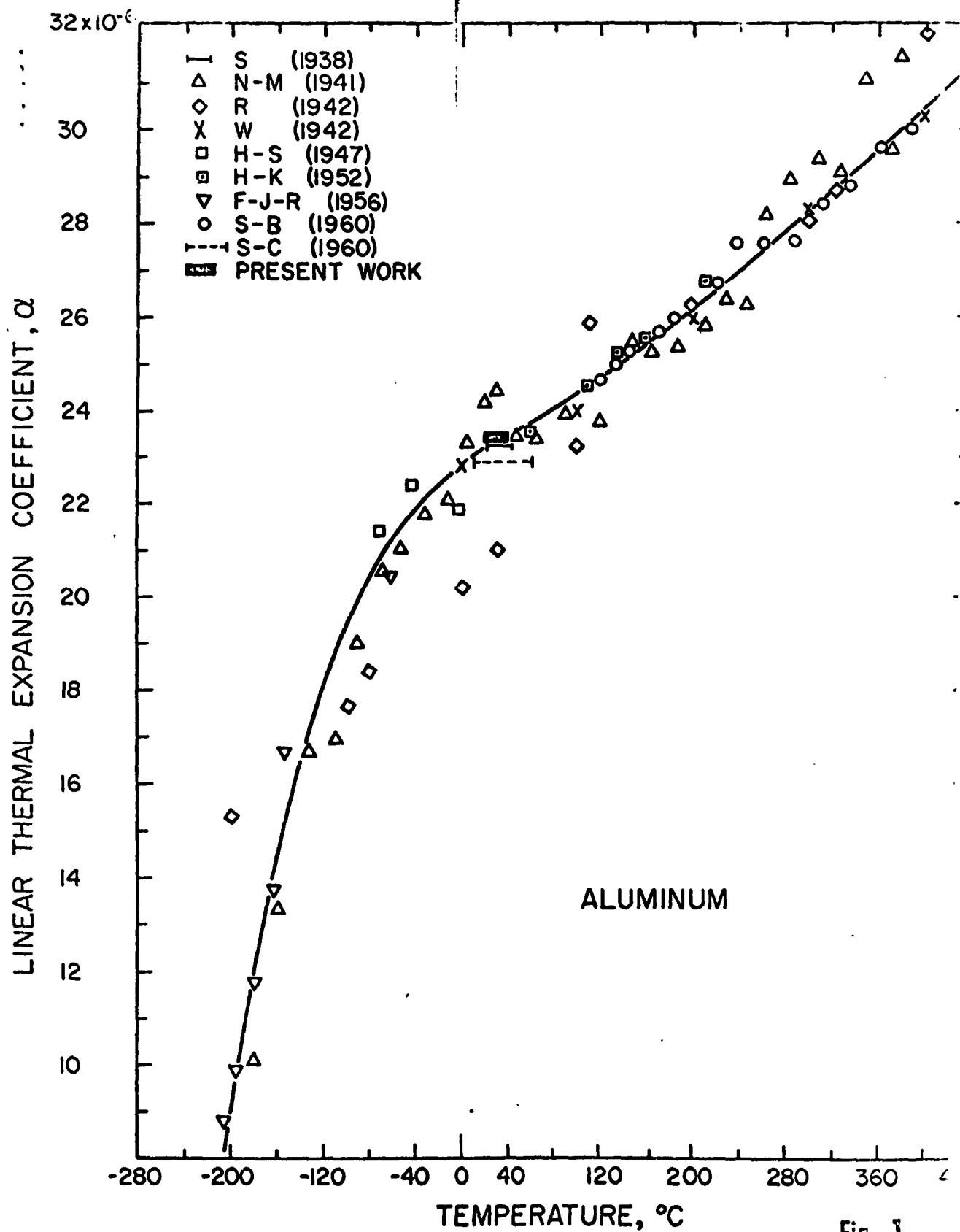


Fig. 1