Branches were able to retain upto 250 ml. copper per sq. meter and it is considered that a volume equivalent to 100 gallons per acre would provide the greatest margin of safety to compensate for inaccuracies in application. In East Africa there have been reports of increased coffee berry disease with increasing number of sprays, which may be due to increased leaf retention creating favourable microclimate for the multiplication of the pathogen.

Insufficient application, wrong timing and dosage, all these invariably result in a disease incidence greater than on trees which have not been sprayed at all. Strange as it might appear this is nevertheless true. Maybe this is a result of retention of infected leaves with heavy source of inoculum, which otherwise would have normally fallen. In India the close spacing of coffee and the forgotten practice of pruning make leaf disease control extremely difficult and perhaps ineffectual. The following few suggestions deserve critical reconsideration as far as the new malady is concerned :

(1) Establishment of the causative agent and its life-cycle.

(2) What is the optimum time, quantity of copper to be put in ? Maybe 3 full sprays are necessary, the first being a pre-blossom one.

(3) It may be necessary to increase the number of spraying to 4 to 5 as the residual effect of copper formulations wear off in 3 to 4 weeks. A clearer picture can emerge only when we have decided upon the optimum spacing of the bushes. Trials are necessary to find if the degree of leaf retention has anything to do with the freedom from the new malady.

(4) Protection of leaves from the ravages of pests such as thrips at a time when bushes which have suffered heavy defoliation or bushes which have been heavily pruned are recovering.

(5) Manurial requirements of coffee under different conditions to offset the disadvantages of heavy carbohydrate drain during an acute leaf disease incidence or heavy crop or both. Apart from mere soil analysis data the need for plant analysis is stressed.

(6) The need for a thorough investigation of optimum shade requirements for coffee in different districts in South India and a reassessment of the necessity of pruning bushes on individual merit as a corrective sanitation practice.

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IMPACT OF QUENCHING FROM MELT ON EQUIATOMIC ALUMINIUM-GERMANIUM ALLOY

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ABSTRACT

Rapid solidification of equiatomic aluminium-germanium alloy is shown to result in the formation of a new non-equilibrium intermediate phase that can be indexed on the basis of a large tetragonal cell ($a = 14.98$ Å, $c = 16.03$ Å, $c/a = 1.070$) with a possible 208 atoms. The structure of this phase is discussed in relation to the equilibrium f.c.c. solid solution.

INTRODUCTION

QUENCHING of liquid metals and alloys at extremely high cooling rates (10^8 to 10^9 deg.c/sec) has been shown to lead to the formation of a large number of new intermediate phases, supersaturated solid solutions and micro- crystalline as well as amorphous phases, in various binary and ternary systems. This technique, generally referred to as 'liquid quenching', 'splat quenching', or 'splat cooling', has been found very effective in filling up gaps in metallurgical equilibrium diagrams, which

according to the well-known Hume-Rothery Rules for alloying should contain electron compounds at certain fixed electron concentrations per atom. A number of such Hume-Rothery compounds have been synthesized in many of the noble metal systems and a large number of reviews[1-4] are presently available on non-equilibrium phases obtained by quenching from the melt.

The aluminium-germanium system is a simple one featuring a eutectic reaction at 424° C. and 30·3 at.% Ge. The maximum solid solubility of Ge in Al is 2·8 at.% at the eutectic temperature and Ge has been reported[5] to disslove a maximum of 0·93 at.% Al at 575° C., i.e., well above the eutectic temperature. Predecki et al.[6] reported briefly on the formation of a complex unidentified phase in a rapidly solidified Al-30 at.% Ge alloy. The structure of this phase has been shown by us[7] to be tetragonal with $a = 13·03$ Å, $c = 12·04$ Å and $c/a = 0·924$. A similar structure has very recently been reported by Ramachandrarao and Anantharaman[8] for a non-equilibrium phase obtained by splat-cooling a Au-27 at.% Ge alloy.

We report here on the formation of another intermediate phase in the Al-Ge system, which occurs on subjecting an Al-50 at.% Ge alloy to rapid solidification.

EXPERIMENTAL PROCEDURE

The equilibrium Al-Ge alloy was prepared in the same way as described earlier.[7] After melting the alloy, it was given a homogenization anneal in vacuum at 300° C. for 120 hours. The technique of rapid quenching from the melt has been described earlier.[7] In the present investigation it consisted of loading 20–50 mg. of the alloy into a graphite crucible with a nozzle below, which was preheated with the aid of a resistance furnace to 700° C., about 60° C. above the liquidus temperature for the alloy. The molten droplet of the alloy was then shot onto a highly polished copper substrate kept at room temperature by means of a shock wave generated by the rupture of a mylar diaphragm with argon gas at a pressure of 500 lb./sq. in. The resultant products were very thin foils of varying thickness and could be easily removed from the substrate by gently tapping the latter. The whole process does not seem to introduce any plastic deformation in the sample. In some regions, the foil was thin enough (< 1000 Å) for direct electron-microscopic examination.

X-ray specimens could be prepared by sticking flakes of the quenched alloy onto a glass fibre with the help of 'Quick Fix'. Debye-Scherrer photographs were recorded in a Philips 114·6 mm. diameter camera with nickel-filtered CuK_α radiation ($\lambda_{CuK\alpha} = 1·54051$ Å). The interplanar spacings were arrived at from an average of 3 or 4 readings, each recorded after applying correction for film shrinkage.

TABLE I

Observed and calculated $sin^2\theta$ values for the non-equilibrium phase in aluminium-50 at.% germanium alloy

Structure : Tetragonal
Lattice parameter : $a = 14·98$ Å $\simeq \sqrt{13}\ a_{FCC}$
$c = 16·03$ Å $\simeq 4\ a_{FCC}$
$c/a = 1·070$

hkl	$sin^2\theta$cal.	$sin^2\theta$obs.	Iobs.
040	0·0423	0·0433	vvw
133	0·0473	0·0474	w
024	0·0475		
042	0·0515	0·0514	vw
240	0·0529	0·0545	s
115	0·0631	0·0631	vvw
333	0·0684	0·0661	w
151	0·0711	0·0726	ms
440	0·0846	0·0846	s
117	0·1186	0·1172	w
084	0·1322	0·1333	vvw
460	0·1375	0·1385	vw
371	0·1557	0·1552	vw
028	0·1586	0·1596	vw
446	0·1679	0·1677	vw
373	0·1742	0·1738	vw
464	0·1745		
266	0·1890	0·1882	vvw
282	0·1891		
119	0·1926	0·1957	vw
571	0·1980		
480	0·2116	0·2124	vvw
284	0·2169	0·2169	vvw
664	0·2274	0·2256	ms
068	0·2433	0·2465	vvw
177	2·2456		
484	0·2486		
680; 0, 10, 0	0·2645	0·2679	ms
377	0·2667		
359	0·2773	0·2787	w
773	0·2800		
4, 10, 0	0·3068	0·3087	vvw
577	0·3091		
088	0·3173	0·3178	vvw
288	0·3279	0·3295	vvw
197	0·3302		
668	0·3385	0·3391	vw
880	0·3386		
46, 10	0·3688	0·3662	vvw
04, 12	0·3754	0·3759	vvw
884	0·3756		
688; 0, 10, 8	0·4125	0·4115	vvw
28, 10	0·4145		

s = strong;   ms = medium strong;   w = weak;
vw = very weak;   vvw = very very weak.

EXPERIMENTAL RESULTS

The X-ray powder photographs revealed a large number of extra reflections along with comparatively weaker reflections from the equilibrium Ge solid solution. Some of the extra reflections were diffuse, but reliable estimates of interplanar spacings could be arrived at by taking several readings from different films. All the extra reflections could be satisfactorily indexed on the basis of a tetragonal unit cell with $a = 14 \cdot 98$ Å, $c = 16 \cdot 03$ Å and $c/a = 1 \cdot 070$. Table I brings out the good agreement between the observed and calculated values of $\sin^2\theta$ for this new structure. Only the first thirty reflections along with their intensities are recorded in this table.

The extra reflections due to the new phase disappeared completely after short annealing treatments at 300° C. and the X-ray patterns reverted to those from a mixture of the two equilibrium phases.

DISCUSSION OF RESULTS

The present investigation has again brought out the tremendous potentiality of the splat-cooling technique in producing new intermediate phases in alloy systems. The structure reported here pertains to the second non-equilibrium phase so far discovered in the Al-Ge system, the first one being the phase reported by us earlier.

Just like the earlier tetragonal structure reported for the Al-30 at.% Ge alloy,[7] the present structure may also be considered as related to the parent Al-solid solution (Fig. 1). The face diagonal of the rectangle obtained by stacking three f.c.c. unit cells in one direction and two f.c.c. unit cells in a direction perpendicular to the same may be taken to constitute the 'a' parameter of the tetragonal unit cell (*i.e.*, $a_{\text{tet}} \simeq \sqrt{13}\ a_{\text{FCC}}$). The 'c' parameter is approximately four times the f.c.c. lattice parameter (*i.e.*, $c_{\text{tet}} \simeq 4a_{\text{FCC}}$). It is clear from Fig. 1 that reflections characteristic of the f.c.c. structure (*i.e.*, all odd or all even indices) may be expected to predominate, if not occur exclusively. Table I shows, in fact, that the f.c.c. extinction rules are strictly followed.

Assuming that the new tetragonal structure displays the same packing efficiency as the f.c.c. solid solution, its unit cell made up of 52 f.c.c. unit cells ($\sqrt{13} \times \sqrt{13} \times 4$) may be expected to contain (52×4), *i.e.*, 208 atoms per unit

cell. On this basis the mean atomic volume for this structure works out to $17 \cdot 3$ Å,[3] which is almost identical with the extrapolated atomic volume ($17 \cdot 4$ Å^3) for a hypothetical
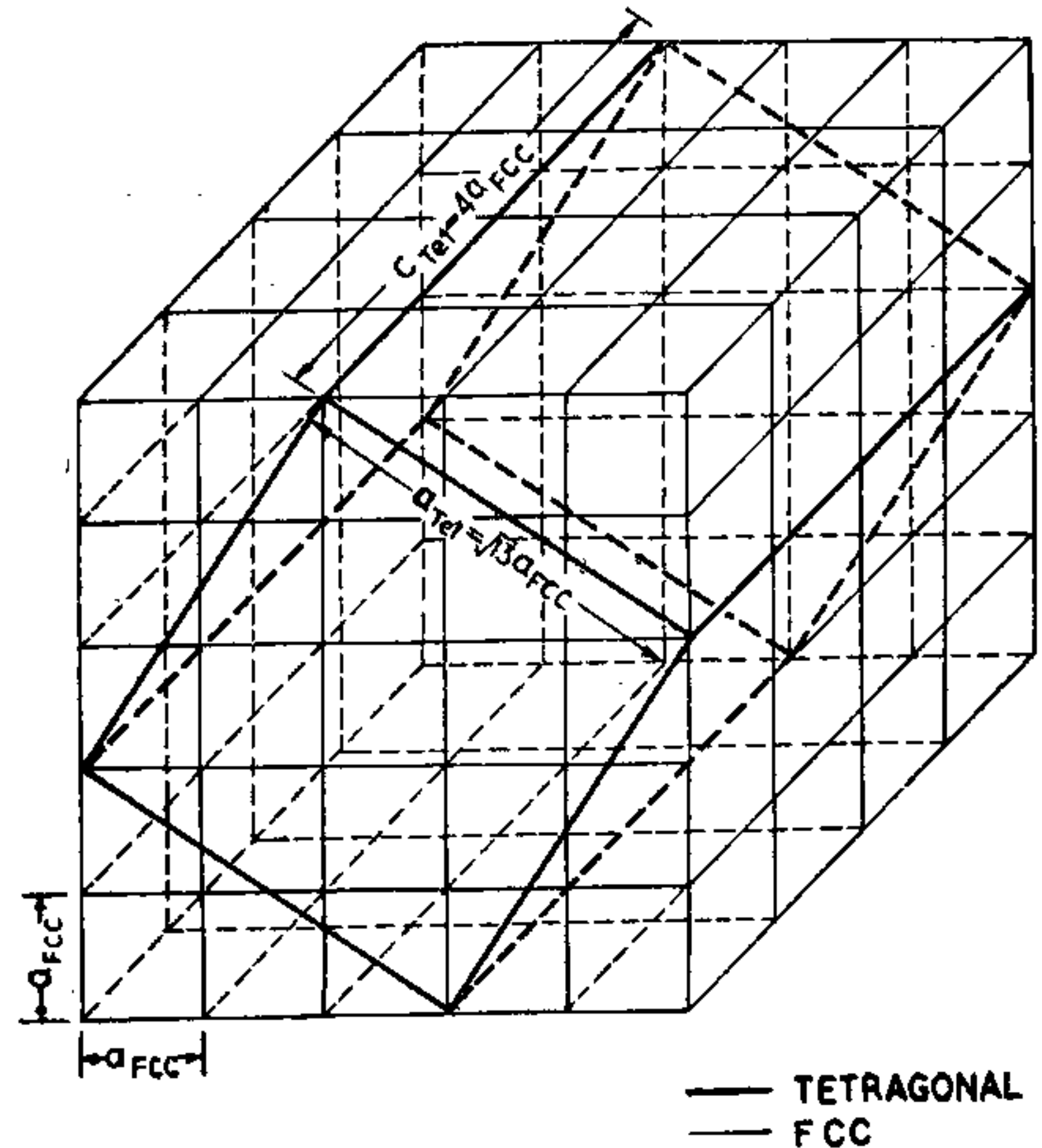

— TETRAGONAL
— FCC

FIG. 1. Formation of the large tetragonal unit cell of the new Al-Ge phase with $a_{\text{tet}} \simeq \sqrt{13}a_{\text{FCC}}$ and $C_{\text{tet}} \simeq 4a_{\text{FCC}}$ from 52 unit cells of the f.c.c. solid solution.

f.c.c. Al-50 at.% Ge alloy.[9] It is worth recalling in this connection that such an assumption on close packing has successfully explained the structural characteristics of not only the Al-Ge phase reported by us earlier,[7] but also quite a few non-equilibrium phases in the Ag-Ge and the Au-Ge systems.[1]

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