# SOME RELATIONSHIPS BETWEEN THE ELECTRON DENSITY OF STATES AND THE METASTABLE STATES OF AlMgSi ALLOYS

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We studied the electron density of states of AlMgSi alloys—receiving solution heat treatment and were quenched—as a function of ageing time at room temperature. Directly after quenching, the Fermi level shifts by 0.8 eV, from 72.8 eV to 72.0 eV. The density of states around the $K$ and $W$ Brillouin zona symmetry points decreased. In the medium energy range the intensity curve elevated and does not contain changes indicating fine structures. Increasing the period of ageing in room temperature causes the SXES curve to gradually approach the SXES curve of pure Al. From both the DTA and the SXES tests we can come to the conclusion that the intensive section of the low temperature G.P. zone formation is maintained in the metastable AlMgSi until the SXES intensity curve fairly well approaches the intensity distribution of the pure Al SXES.

In the literature many studies are found concerning the investigations of dilute AlMgSi alloys which had received solution heat treatment and quenching.[1] It is a well known fact that the AlMgSi alloy which received solution heat treatment above 780 K temperature and then was quenched in liquid at room temperature, forms a super-saturated metastable solution. At room temperature immediately after quenching, the low temperature G.P. zone formation begins to develop with a rather high speed.[2]

This procedure, which takes place by diffusion, can continue for even some weeks at room temperature, but more than 2/3 of the formed zones are produced during the first two days of the ageing time. An essential property of the zones is that at room temperature they practically remain for an optional period of time. In this metastable state the alloy has a few advantageous properties.

The zone formation process in AlMgSi alloys has been shown by electric conductivity[3] and microhardness[4] measurements.

Interesting considerations were formed regarding the investigation and explanation of the relationships between lattice defect and zone formation. The interaction between the dislocations and the individual alloying atoms was investigated among others by McGroove.[5] In an earlier work[4] we had formed our opinion in connection with the development of G.P. zones, that besides the significance of the role of vacancies and dislocations the interactions between the atoms themselves can also be important factors in the mentioned processes. According to our assumption the common influences of these factors creates these particular crystal defects (G.P. zones).

In our present work we paid the greatest attention to the changes that take place in the electron structure after quenching, and we attempted to investigate their behaviour during the periods immediately following quenching.

## EXPERIMENTAL METHOD

For the measurement of density of electron states we used the soft X-ray emission spectroscopy (SXES) method. The main point of the well known method[6] is that from the characteristic X-ray radiation we can deduce the proper density of states, taking into consideration the quantum-mechanical selection rules and the transitional probabilities.

The equipment is of the RSM 500 type (Burevestnik, Leningrad), with grating mirror design, and working in the 0.5–50 nm range is a factory device. The detailed description of the equipment was given by Lukirskii, Brytov and Komiak.[7] The resolving power of the equipment in the range of our measurements was 0.3 eV.

We measured the AlMgSi alloy with radiation relative to the Al $L_{2,3}$ level. The excitation electron beam was 5 kV, 0.3 mA.

The differential thermo-analysis (DTA) investigations used for control measurements, was performed with a sensitive, specially designed instrument.[8]

The composition of the sample was: Al matrix, 0.58 wt% Mg, 0.38 wt% Si, 0.14 wt% Fe.

## EXPERIMENTAL RESULTS

For studying the changes caused by the alloy it seemed advisable to use the SXES curve of pure aluminium (99.99%) as a reference on our equipment (Figure 1). On the figure—which is in exact agreement with the curve known from the literature[9]—we plotted the adequate positions for the most important symmetry points according to Rooke[10] and Singhal and Callaway.[11]

On Figure 2, we can see the emission diagram of an AlMgSi alloy heat treated for 45 minutes at 800 K and then quenched in liquid at room temperature, which diagram was plotted immediately after quenching and was compared to pure Al. By comparing the two curves we can see that the emission edge (72.8 eV) shifted by 0.8 eV ± 0.3 eV, the peak below the edge de-
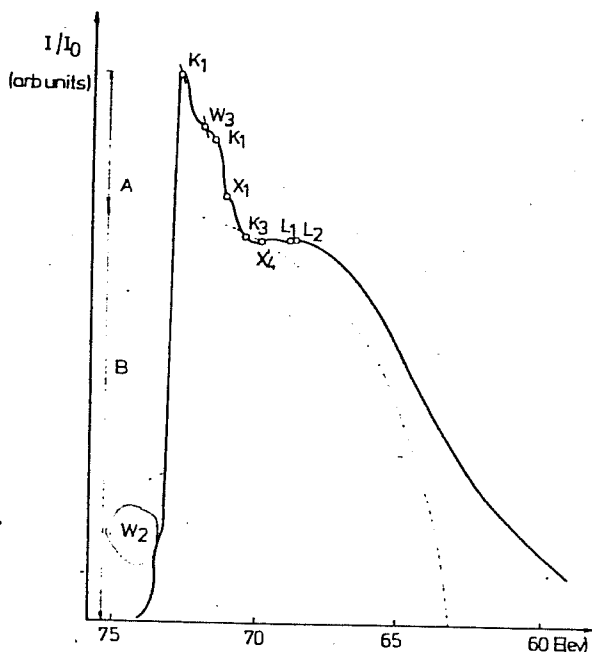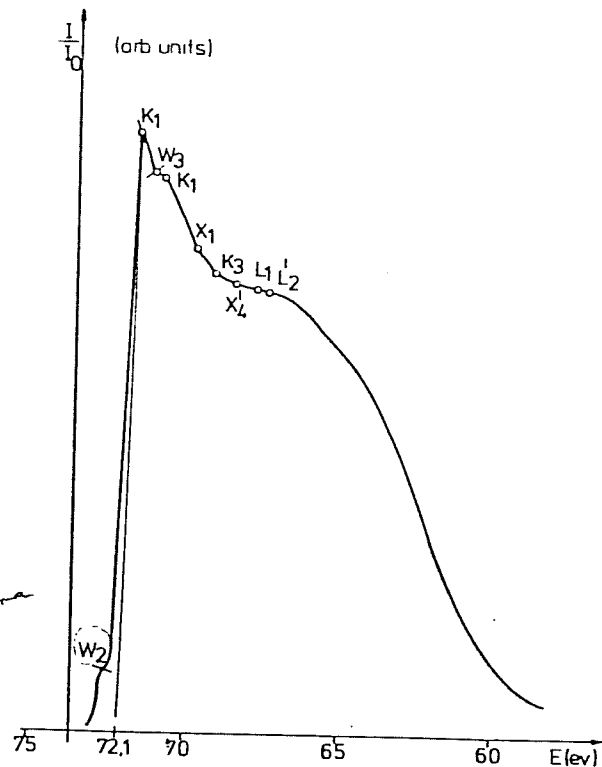


FIGURE 2 The SXES curve of an AlMgSi alloy heat treated for 45 min at 800 K and quenched (solution heat treatment).

creased and after this the curve gradually decreases towards the smaller energy values. The finer changes found with Al do not appear in this case in this section.

Figures 3, 4 and 5 show the SXES diagrams as a function of time of heat treating at 500 K by electron beam compared to the Al reference diagram.

Figure 3 curve a. shows the diagram of pure Al, Figure 3 curve b. the state of the AlMgSi alloy receiving solution heat treatment, was quenched and measured after 10 minutes duration, Figure 3 curve c. shows the test after 20 minutes, Figure 3 curve d. after 30 minutes, Figure 4. curve a. is the reference again, Figure 4. curve b. shows the measurement after 40 minutes, Figure 4 curve c. after 50 minutes, and finally Figure 4 curve d. shows the measurement performed after 60 minutes duration. Figures 5 curve a is the reference again, curve b alloy after 70 min ageing, curve c after 80, curve d after 120 minutes.

We can establish the fact that with time the



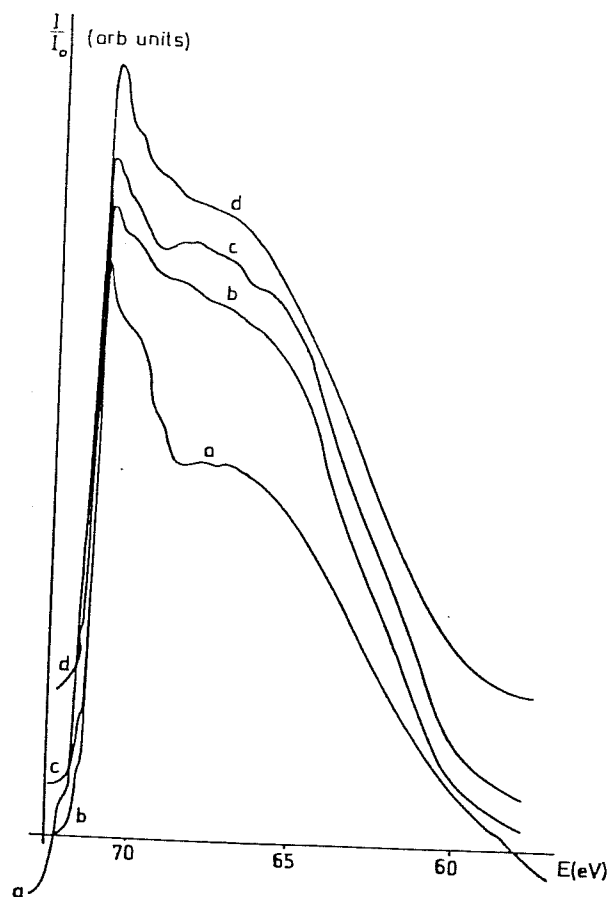FIGURE 1 The SXES curve of pure Al as reference.

I/I₀ (arb units)

FIGURE 3 The SXES curves: (a) of pure Al (reference) (b) of AlMgSi alloy after solution heat treatment measured for 10 min (c) measured for 20 min (d) measured for 30 min.

curves gradually approach the corresponding diagram of the pure, reference—aluminium as a function of time.

It must be mentioned that during the measurements the temperature of the sample deviated from room temperature due to the heating effect of the electron beam. According to our relative measurements,[12] the temperature increase caused some acceleration of the low temperature zone formation, but it did not create other effects.

The SXES diagram made after quenching and two days of natural ageing at room temperature is shown on Figure 6 curve b. (Figure 6 curve a shows the reference, the diagram of pure Al). The large energy emission edge is in agreement with that of pure Al and among the measurements performed until now the whole run of the curve comes nearest to that of the reference

diagram. The largest deviation from the reference is that in the medium energy range the steepness of the curve made of the alloy is higher.

On Figure 7 we present the DTA curves of the alloy received solution heat treatment and quenching, and which was naturally aged for different periods (1 hour, 2 days and 6 days) of ageing time at room temperature.[13] Figure 7 curve a. shows the alloy aged for 1 hour, Figure 7 curve b. the one aged for 2 days and Figure 7 curve c. the alloy aged for 6 days. With the increase of time a vigorous increase of the endotherm process can be seen at 495 K and together with this of the exotherm process too, marked by $N_1$. While after one hour of ageing the appearance of the processes marked by $N_1$ and $N_2$ can be well separated, on the diagram made after 2 days of ageing at room temperature the $N_1$ and $N_2$ effects are superimposed due to the vigorous increase of the effect of $N_1$.

At last two curves are represented in the Figures 8, 9 where the summary of the measure-
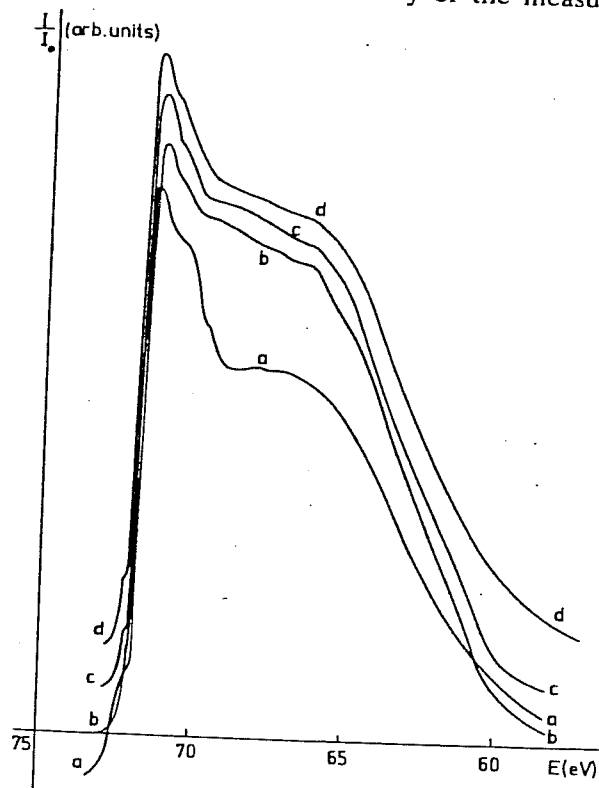
I/I₀ (arb.units)

FIGURE 4 The SXES curves: (a) reference (b) alloy, measured for 40 min (c) measured for 50 min (d) measured for 60 min.

FIGURE 5 The SXES curves: (a) reference (b) alloy measured for 70 min (c) alloy measured for 80 min (d) measured for 120 min.

The Fermi level of the alloy is shifted by 0.8 eV (to 72 eV). At the same time the maximum around the K and W symmetry points of Briolluin zone decreased, and became wider and the fine structure characteristic of the other symmetry points does not appear.

The decreasing of maximum containing states of several bands, together with the continuous intensity decrease without fine structures, indicates a metastable condition resembling liquid state, that is indicates some symmetry changes.

Considering the electron structure of Mg and Si, with such an alloy composition and in the case of complete dilution, the number of electrons in the conduction band decreases by 0.3%. According to the present measurements the shifting of the Fermi level shows a considerably larger change than the above value.

We can assume that the aforementioned two changes may be explained by the increased density of states in the medium energy ranges, since the decrease of the Fermi level and the state of density belonging to the K and W points directly
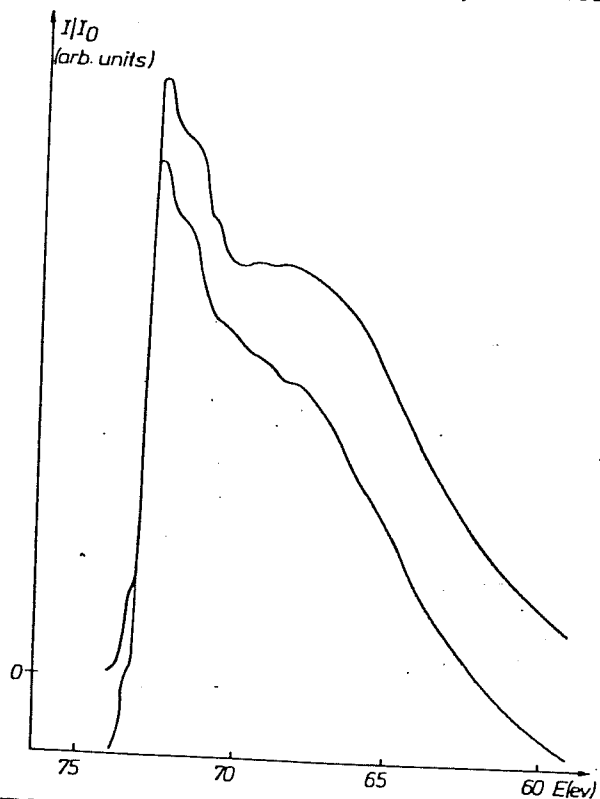
ments are shown.

In the Figure 8 is the change of the Fermi surface as a function of time after solution heat treatment.

In the Figure 9 is the change of the peak occurring straight under the Fermi surface. There is a proportion between the free electron parabolic approximation and the superimposed peak received from the mixed states (A/B in Figure 1)

In each case the curves start to increase approximately after 15 minutes.

## DISCUSSION

The biggest deviation from Al reference is shown by the SXES diagram made of the alloy which received solution heat treatment at 800 K and then was quenched and immediately measured.



FIGURE 6 The SXES curves: (a) reference (b) alloy after solution heat treatment ageing at room temperature 1 day, and after it measured.

exo

$\Delta T$ $\downarrow$ 0,125°K

endo
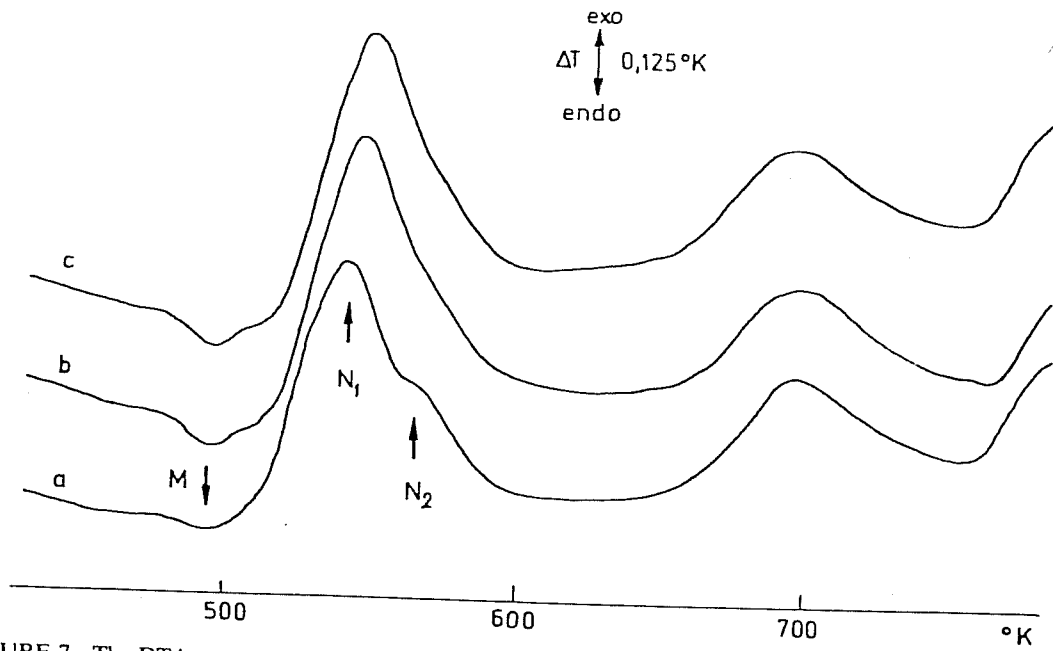
c

b

a

M $\downarrow$

$N_1$

$N_2$

500   600   700   °K

FIGURE 7  The DTA curves: (a) AlMgSi alloy after solution heat treatment ageing at room temperature 1 hour (b) ageing 2 day (c) ageing 6 day.

$E(ev)$

73,0

72,8

72,6

72,4

72,2

72,0
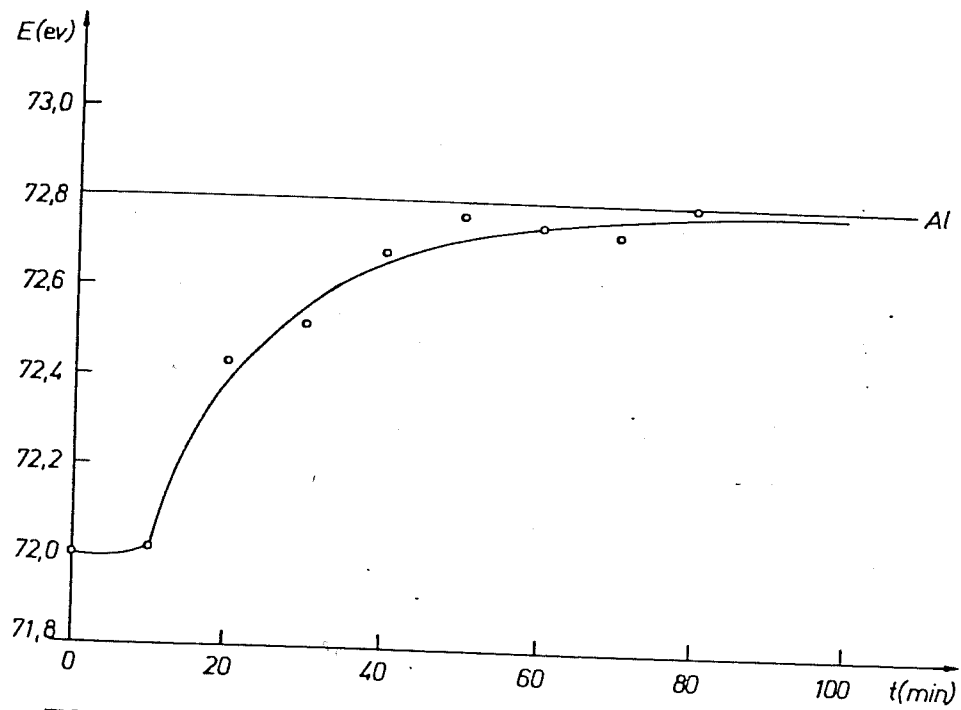
71,8

Al

0   20   40   60   80   100   $t(min)$

FIGURE 8  The change of the Fermi surface versus time after solution heat treatment.
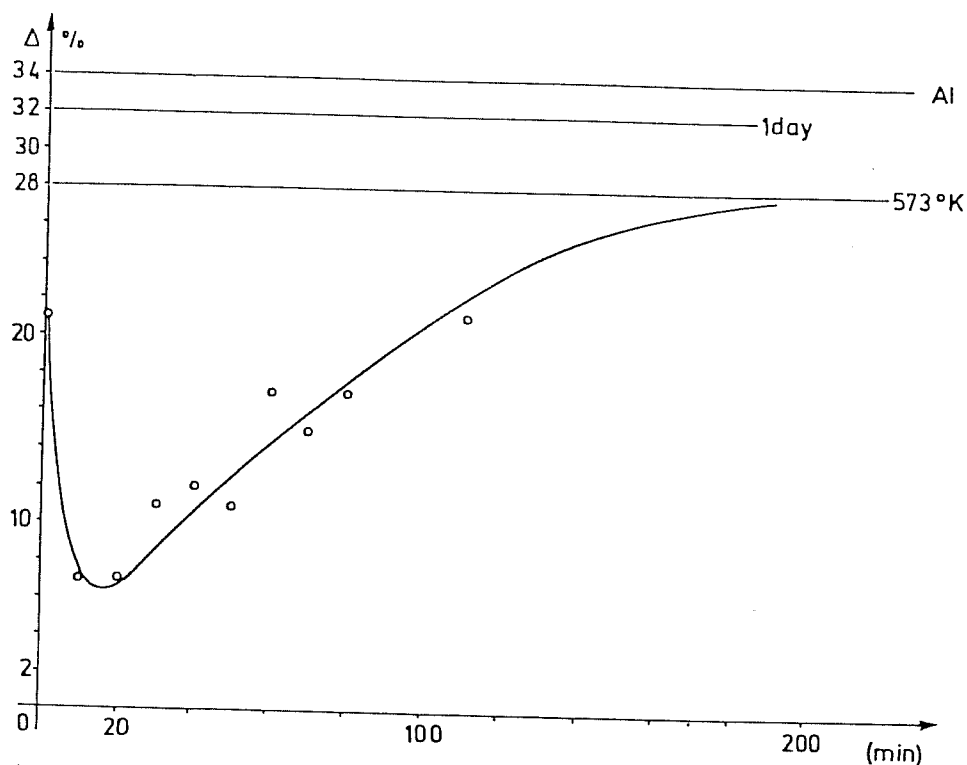
FIGURE 9   The change of the relative peak intensity about K symmetry point is SXES curves.

below it may be compensated by the density of states associated with the medium energy ranges. However, the disappearance of fine structures in this range indicates an approach to the liquid state.

The alloys of different states presented on Figures 3 and 4 show a decrease in the metastable state. The SXES intensities in the appropriate symmetry points as a function of time gradually approach the fine structure of pure aluminium. The remaining small deviation is the "result" of inevitable warming up during the measurement.

The SXES diagram obtained of the alloy after natural ageing, that is after the increasing of the number and size of the G.P. zones, resembles most closely the reference diagrams. From the above it follows that in the metastable state of the alloy the intensive zone formation continues until the symmetries characteristic of Al matrix are restored. As soon as the fine structure characteristic of Al appears, the intensive zone formation stage is also completed.

The results of the presented DTA measurements performed for control are in complete accordance with the SXES measurements. On the DTA curve made immediately after solution heat treatment and quenching, the transformation effect marked by $M$ and characteristic of the transformation of low temperature zones cannot be displayed. In this state the maximums at 543 K and 573 K can be relatively well detected, which maximums are characteristic of the developing medium temperature zones $(N_1)$ and of the effect related to a Si precipitation $(N_2)$.[14]

With the increase of natural ageing time the transformation process marked $M$ also increases continuously, together with the increasing of the medium temperature zone formation marked by $N_1$.[13] Since the increase of $M$ and $N_1$ is in close relationship with the number of low temperature zones, thus the degree of these effects indicates the increase of the number of low temperature G.P. zones.

On the basis of the above information the low temperature zone formation is also in close relationship with the electron structure of the Al matrix.

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