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Effect of Precipitation Hardening on the Superconducting Properties of Aluminum*

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The effect of heat treatment on the superconducting properties of a precipitation hardening Al-Mg-Si alloy has been studied in some detail by ballistic induction techniques. The alloy (Alcoa 6063) contains approximately 1.1% Mg_2Si which precipitates from a supersaturated solid solution to an extent controlled by the heat treatment. The precipitation process results in marked changes in the mechanical properties of the alloy, and equally pronounced changes are found to occur in the superconducting behavior. For heat treatments which produce mechanical properties similar to those of pure Al, the superconducting properties of the alloy are found to be substantially the same as pure Al. Heat treatment to the condition of maximum hardness depresses the critical field of the alloy about 8 gauss below that of pure Al, the effect being closely similar to that expected for the application of hydrostatic pressure. In conditions of intermediate hardness pronounced hysteretic effects are observed. It is proposed that the observed changes arise from coherency stress around the Guinier-Preston zones which describe the aggregation of Mg and Si atoms in the early stages of precipitation.

I. INTRODUCTION

It is well known that alloying additions can produce changes in the properties of a superconducting element and a considerable volume of work on alloy systems has been accumulated.[1] The present work deals with a specialized property of certain alloy systems, being concerned with the changes in superconducting behavior which accompany the various stages of precipitation hardening of an aluminum alloy.

The study of precipitation hardening departs from the practice in previous alloy investigations since the parameter under control may be loosely termed the state of dispersion of the alloying constituents rather than their relative chemical concentration. All of the effects described hereafter may be produced in a single specimen, without altering its chemical analysis, by the relatively simple expedient of controlling its heat treatment.

The present results show that precipitation hardening is accompanied by some rather large and well-defined changes in superconducting behavior. Aside from the question of the fundamental mechanisms responsible for these changes, the results are of interest in suggesting a new technique for studying the progress of the metallurgical transformations which accompany the process of precipitation hardening.

A brief preliminary report of this work appeared some time ago.[2] However, the full details, which seemed discouragingly complex at the time, have been withheld pending the formulation of a reasonably adequate physical explanation of their significance.

II. PLAN OF THE EXPERIMENT

The present work was intended as an exploratory study of the effect of the precipitation hardening process on the superconducting properties of an alloy. The specimens used were prepared from a commercial alloy (Alcoa 6063) which is >98% Al plus Mg and Si in the approximate stoichiometric proportions of Mg_2Si. This alloy seemed the best compromise between our self-imposed criteria of high Al content and maximum change of mechanical properties with precipitation hardening.

Precipitation hardening of Al–Mg–Si depends on the fact that the solubility of Mg_2Si in Al varies from about 1.85% at 595°C to about 0.1% at room temperature. Heat treatment is carried out in two stages. The alloy is first heated to place the Mg and Si in solution and then rapidly cooled by quenching to room temperature with the Mg and Si dispersed as a supersaturated solid solution. In the quenched condition the strength and hardness of the alloy are only slightly greater than pure Al.

Specimens may be hardened at a controlled rate by holding them at an elevated temperature, this process being known as aging. The increase in yield strength and hardness of this alloy with aging time is shown in Figs. 1 and 2. At the temperature of the present work the mechanical properties achieve a maximum value for an aging time of about 21 hours.[3] In this condition (fully hard) the mechanical properties of the alloy

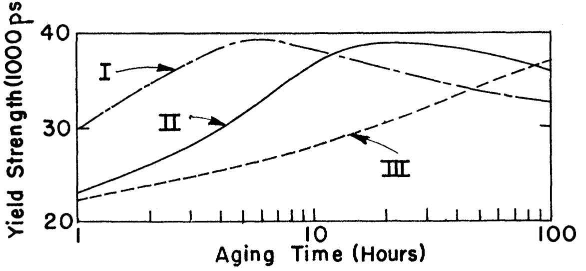

FIG. 1. Yield strength of Al-Mg-Si alloy vs aging time, after Nock.[3] Curves show the effect of different aging temperatures: I-190°C; II-171°C; and III-149°C.

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[1] D. Shoenberg, *Superconductivity* (Cambridge University Press, New York, 1952), 2nd ed.; also B. Serin, *Encyclopedia of Physics XV*, edited by S. Flügge (Springer-Verlag, Berlin, 1956), p. 268.

[2] R. E. Mould and D. E. Mapother, Phys. Rev. **96**, 797 (1954).

[3] J. A. Nock, Jr., Iron Age **159**, 48 (1947).

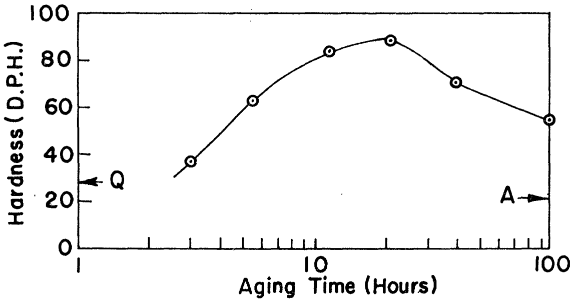

FIG. 2. Diamond pyramid hardness (D.P.H.) vs aging time for Al-Mg-Si alloy as measured in this work. All alloy specimens aged at 175°C. Q and A denote hardness values for quenched and annealed specimens, respectively.

approximate those of a mild steel. With continued aging, both strength and hardness decline and the specimen is then described as overaged.

The superconducting critical-field curve (H_C vs T) from T_C down to about 0.8°K was measured for alloy specimens in various conditions of hardness. Measurements were made by a magnetic method which permitted examination of the magnetic reversibility of the superconducting transition.

III. EXPERIMENTAL DETAILS

A. Cryogenic Techniques

All superconducting transitions were measured under accurately isothermal conditions using a ballistic induction method. The apparatus and techniques employed for the measurements have been fully described in a previous article.[4] The alloy transitions were always compared with the transition of a pure Al control specimen which was maintained at the same temperature by thermal contact with He II.

Temperature measurements were made using a carbon resistor with results which are believed less accurate than later measurements using a magnetic thermometer. However, the absolute temperature is relatively unimportant in the present observations and, in the few instances where an accurate value of T is desirable, the H_C value[5] for pure Al has been used to correct the values deduced from resistance measurements.

B. Specimen Preparation

Specimens used for the superconductivity measurements were machined[6] from commercial bar stock in the form of ellipsoids of revolution with major and minor axes of 2.50 and 0.242 in., respectively. For ellipsoids of this eccentricity the demagnetizing factor is $n=0.0193$,[7] giving an "ideal" transition width (nH_C) about 2% of the critical field. Experimentally, the factor $n=0.014$ has been shown to describe the breadth of the superconducting transition in a pure Al specimen of identical shape with reasonable accuracy.[4] Thus any departure from this expected breadth by the alloy specimens could be attributed to inhomogeneity in the superconducting properties.

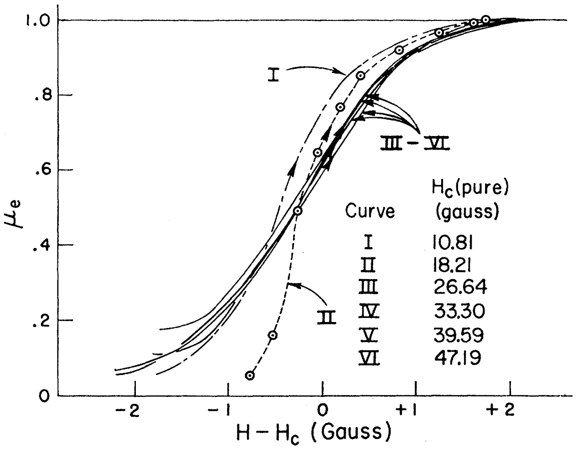

FIG. 3. Magnetic transition curves for quenched Al-Mg-Si alloy. Here (and through Fig. 8) the abscissa gives the difference between the applied magnetic field during the observed transition and the critical field of pure Al. The quenched alloy shows no appreciable shift in critical field.

All alloy specimens were given a solution heat treatment by holding them at 575°C for 24 hr in a helium atmosphere followed by a water quench to room temperature. Aging was done at 175°C for varying lengths of time. Since the quenched alloy ages slowly even at room temperature, specimens to be studied in the quenched or slightly hardened conditions were stored in liquid nitrogen until used. The same specimens were reused for measurements in different conditions of hardness, being carried through the entire heat treatment for each use. Both the hardness and the superconductivity measurements showed that the recycling produced no detectable progressive effect.

As indicated in Fig. 1, very long times are required to reach equilibrium in the precipitation process at an aging temperature of 175°C. A more expeditious procedure for obtaining a soft but thoroughly precipitated condition consists in cooling the specimen slowly from 575°C. Specimens which are strongly overaged by this procedure will be described as annealed.

As received, the alloy specimens had been heavily cold worked so that on the first solution heat treatment considerable grain growth occurred. A macro-etch of the specimens after quenching showed the grain size to be

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[4] J. F. Cochran, D. E. Mapother, and R. E. Mould, Phys. Rev. **103**, 1657 (1956).

[5] J. F. Cochran and D. E. Mapother, Phys. Rev. **111**, 132 (1958).

[6] Attempts to recast the alloy specimens as single crystals were found to remove the Mg (but not the Si) from the alloy. Faced with this development it was decided to make the measurements on polycrystalline specimens. The results showed no evidence that the presence of grain boundaries had any appreciable effect on the superconducting behavior.

[7] E. C. Stoner, Phil. Mag. **36**, 803 (1945).

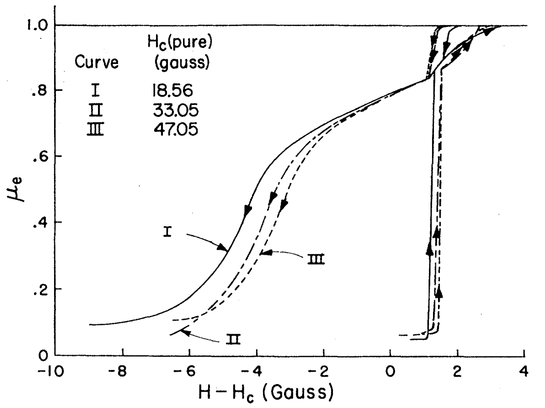

FIG. 4. Magnetic transitions for alloy aged 5.5 hr at 175°C. Substantial hysteresis is now evident in the *N-S* transition and the *S-N* transition occurs at fields above H_c (pure). Permeability values in the *N-S* transition show that >50% of the specimen volume participates in the delayed transition near $H-H_c=-4$ gauss. Experimentally the *S-N* transitions in the underaged condition seem discontinuous since no points could be obtained in the steep initial rise near H_c(pure). (The same is true of the corresponding transitions in Fig. 5.)

about 1 to 3 mm. No further grain growth was observed on subsequent reheating.

Test specimens of the alloy were heat treated together with the ellipsoids and their hardness determined in terms of the Vickers Hardness Number (D. P. H.).[8] The results of these determinations are given by the points shown in Fig. 2. Hardness tests were made only to check that the alloy was responding to the heat treatment in the usual manner, and no attempt is made to attach any further significance to the values obtained.

Chemical analysis of part of a specimen used in the measurements showed the following elements in addition to Al: Mg(0.63); Si(0.31); Fe(0.16); Cu(0.02); Zn, Cr, Ti, less than (0.01). All of the numbers in parentheses are in weight percent, and these values lie well within the composition limits given by the Aluminum Company of America for this alloy.

Attempts at x-ray determination of the lattice parameter of the alloy gave very poor results owing to difficulties associated with surface preparation of the specimens. The results agreed qualitatively with but added nothing to the picture presented in the earlier work of Gayler and Preston.[9]

The electrical resistivity of the alloy was determined using standard dc potentiometric techniques on specially prepared 0.020-in. diam wire specimens.[10] The measurements may be described in terms of the resistance ratio $\rho=R_0/R_{273}$ (ideal), where R_0 is the residual resistance (usually measured at 4.2°K but here measured near 6°K for technical reasons). R_{273} (ideal) denotes the so-called "ideal" resistance at 273°K (obtained by subtracting the residual resistance from the measured resistance at 273°K). The value for ρ for the alloy was about 0.2 ($\pm 15\%$) in both the quenched and fully hardened conditions. To the accuracy of these measurements no systematic difference in the values of ρ was seen between the quenched and hardened conditions. Similar (but more accurate) measurements on a specimen of the pure Al used as the standard gave $\rho=0.0022\pm0.0001$, indicating a relatively high purity.

The preparation of the pure Al standard specimens was identical in all respects (including ellipsoidal shape) to that of the single crystals described in an earlier report.[4]

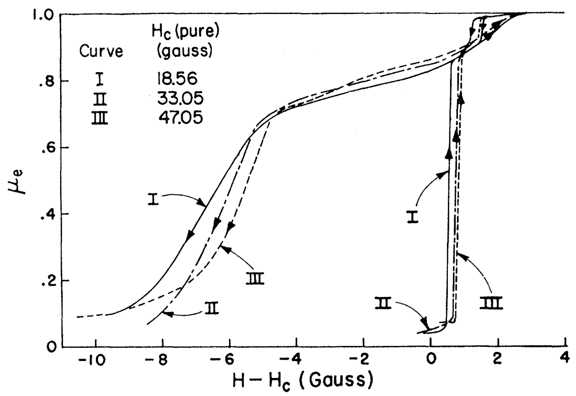

FIG. 5. Magnetic transitions for alloy aged 8.5 hr at 175°C. "Knee" in the *N-S* transition now occurs at lower fields and a larger fraction of specimen volume participates in the delayed transition.

IV. RESULTS

A. Magnetic Transitions

The detailed results of the investigation are presented in Figs. 3–8 in all of which the effective permeability, $\mu_e=B/H_{c'}$[4] is plotted as a function of $(H-H_c)$. Here H

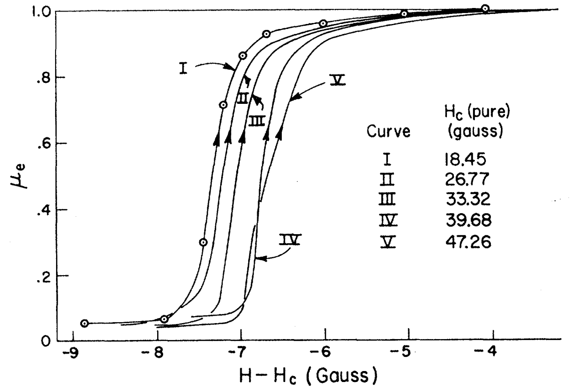

FIG. 6. Magnetic transitions for alloy aged 11.5 hr at 175°C. Note that the position of the *S-N* transition has shifted downward by about 7 gauss from the position shown in Fig. 5. Some hysteresis is still present (see top diagram of Fig. 9) but it is greatly reduced.

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[8] G. L. Kehl, *The Principles of Metallographic Laboratory Practice* (McGraw-Hill Book Company, Inc., New York, 1943), pp. 196–200.

[9] M. L. V. Gayler and G. D. Preston, J. Inst. Metals **41**, 191 (1929).

[10] Unpublished measurements of B. S. Chandrasekhar.

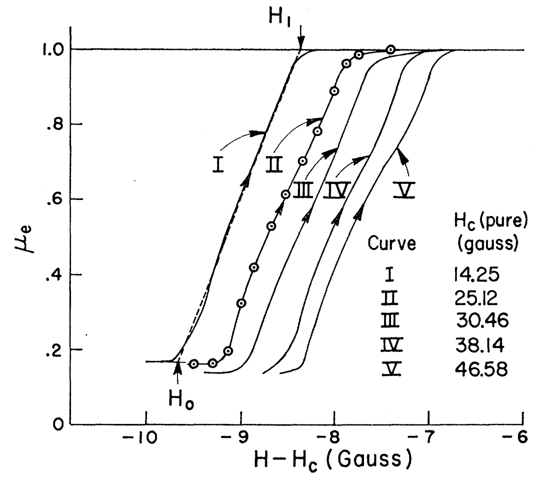

FIG. 7. Magnetic transitions for alloy aged 21 hr at 175°C (fully hardened condition). The *S-N* transition now shows its maximum displacement from H_c (pure). Hysteresis is very small (see top diagram of Fig. 9). Numerical data for 12 transitions in the fully hardened condition are given in Table I and include the 5 transitions shown here.

is the applied magnetic field at which the plotted value of μ_e was observed, and H_c is the critical field of pure Al for the temperature at which the alloy transition was measured. Plotting in this way makes it possible to display transitions for the entire temperature range in one figure and to show the transitions in considerable detail by using an expanded scale for the abscissa.

Each figure shows transitions for the alloy in one condition of hardness and contains essentially all the data obtained on a single experimental run. The numbering of the figures is arranged to show the effect of increasing aging time. For most of the transitions shown, experimental points have been omitted for clarity of illustration. To indicate the detail with which measurements were made and also the fidelity with which the plotted curves reproduce the data, experimental points are shown for typical curves on some of the figures. It will be seen that all points lie on the curves as drawn. This is also true for the curves whose points are not specifically shown.

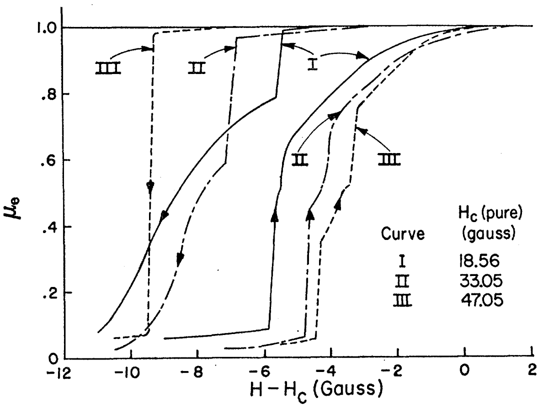

FIG. 8. Magnetic transitions for alloy aged 100 hr at 175°C. Alloy is distinctly overaged but still retains substantial hardness (see Fig. 2). Large hysteresis is again evident but of a different pattern from that observed in the underaged condition (compare Figs. 4 and 5).

Figure 3 presents the transitions of the alloy in the quenched condition. All transitions shown were measured with increasing magnetic field (*S–N* transition),[11] but a typical *N–S* transition is shown for the quenched condition in the isothermal summary plot of Fig. 9. In Figs. 3–8 the individual transitions are numbered in order of decreasing temperature, but in Fig. 3, curves III–VI have not been distinguished from each other since they differ at most by about 0.15 gauss, which is within the possible error in H.

The observed minimum values of μ_e in the transition plots are generally larger than zero and correspond to the fact that a somewhat variable amount of magnetic flux is "frozen" in the specimens following the first *N–S* transition in finite H. This is an effect which, in our experience, is always present to some degree even with pure specimens. However, it does not have any significant influence on the shape of the transition aside from the shift in the origin of the μ_e axis. This assertion has been checked experimentally by studying transitions where the specimen was cooled from above T_c in zero magnetic field. When this is done there is no flux to be frozen in and the specimen initially has $\mu_e=0$. For specimens cooled in this way the *S–N* transitions agree very well with those observed by cycling the specimens magnetically into the normal state and back. The latter method was used for most of the present work since the temperature cycling necessary to completely eliminate trapped flux is very time consuming.

In connection with Fig. 3 the following points should be noted for comparison with the behavior shown on the subsequent figures:

(a) *No critical field shift.* The transitions are all closely centered at $H=H_c$. Thus the quenched alloy has substantially the same critical field as pure Al.

(b) *Transition width.* The transition width for the quenched alloy is about 2.5 gauss and is substantially independent of temperature. This differs from the behavior of pure Al where transition widths in reasonable accord with the demagnetizing factor are observed over most of the superconducting temperature range. In view of the expanded scale of Fig. 3, this is not a major effect and much greater broadening is commonly observed in alloys.

(c) *Hysteresis.* To avoid confusion, no *N–S* transitions are shown in Fig. 3, but a typical *N–S* transition given

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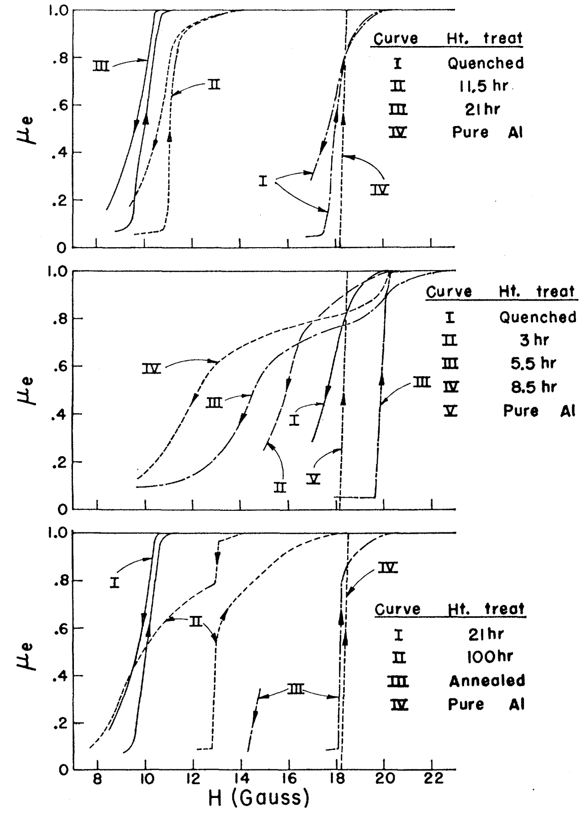
[11] Here and throughout this article we use the abbreviations, *S-N* and *N-S*, to denote the direction of change of the superconducting transition in the specimen. The notation *S-N* denotes a transition from the superconducting to the normal state or, what is always equivalent, a transition in increasing applied field.

in Fig. 9 shows that the quenched alloy exhibited very little hysteresis.

The evolution in superconducting behavior which accompanies the advance of the precipitation process is plain from the sequence, Figs. 3–8. Some additional notes on particular features of the various states of hardness are included in the figure captions.

In Fig. 9 permeability plots for all the measured conditions of heat treatment are presented. These transitions were all measured at the same temperatures and all are plotted vs the actual applied magnetic field.

The evolution of the successive stages in the magnetic transitions (with increasing aging time) may be traced in Fig. 9. The upper plot shows the relatively sharp transitions observed in the limiting conditions of the alloy as quenched and when approaching full hardness. The hysteresis which develops as a result of the downward displacement of the N–S transition in the early stages of aging is summarized in the middle plot. The lower plot illustrates the distinctive hysteresis observed when the alloy is overaged. When overaging is sufficient to anneal the alloy, the S–N transition returns to near coincidence with that of pure Al.



Curve	Ht. treat
I	Quenched
II	11.5 hr
III	21 hr
IV	Pure Al

Curve	Ht. treat
I	Quenched
II	3 hr
III	5.5 hr
IV	8.5 hr
V	Pure Al

Curve	Ht. treat
I	21 hr
II	100 hr
III	Annealed
IV	Pure Al

FIG. 9. Summary plot of alloy transitions for various heat treatments. Numbers in tables denote aging time at 175°C. All transitions were measured at the same temperature ($T\sim1.08$°K) and plotted against the applied magnetic field. Curves II (middle diagram) and III (lower diagram) describe heat treatments not shown in the preceding figures.

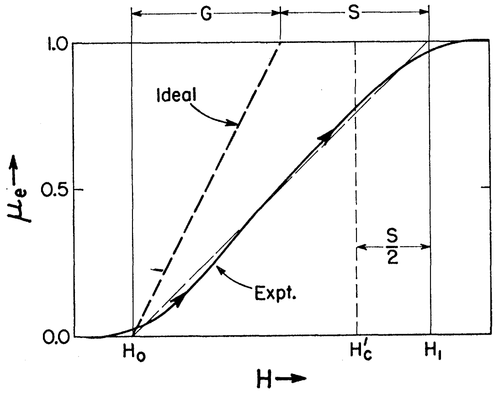


FIG. 10. Schematic diagram illustrating definition of the average critical field, H_c', for the alloy in the fully hardened condition. G is the transition width expected on the basis of the specimen's demagnetizing factor.

Two conditions of heat treatment not shown in the previous figures appear in Fig. 9. The N–S transition of a specimen aged for 3 hr is shown in the middle plot. The S–N transition for the 3-hr specimen (and also the 8.5-hr specimen) is omitted because of its similarity to the S–N transition of the 5.5-hr specimen. The bottom plot shows the S–N transition of an annealed specimen which is seen to coincide closely with the pure Al transition. N–S transitions were not measured in detail for the annealed specimen. Rough measurements showed the annealed specimen to exhibit some supercooling and that the transition was complete at a field about 4 gauss less than H_c for pure Al, as indicated by the fragmentary N–S curve in Fig. 9.

B. Definition of H_c for the Hardened Alloy

The transition width of the hardened alloy specimens is significantly larger than that to be expected on the basis of the demagnetizing factor. This is probably due to inhomogeneity of stress within the alloy, a condition which in varying degree must infect the alloy at all stages of heat treatment. Whatever the cause, the occurrence of broadened transitions raises the question of a suitable definition of the average critical field for the alloy in the fully hardened condition.

Figure 10 gives a schematic illustration of the principle followed in defining the average critical field, H_c'. In Fig. 10, H_0 and H_1 are the experimentally determined limits of the S–N transition. (A typical set of H_0 and H_1 is shown on curve I of Fig. 7.) However, part of the interval $(H_1\text{–}H_0)$ results from geometrical broadening due to n, the demagnetizing factor of the ellipsoidal specimen. In Fig. 10 the geometrical breadth G is determined by constructing an "ideal" transition from H_0 with slope corresponding to n, or analytically, from the relation, $G=nH_0/(1\text{–}n)$. The remaining transition breadth is $S=(H_1\text{–}H_0)-G$, and is characteristic of the specimen. The average critical field of the alloy is

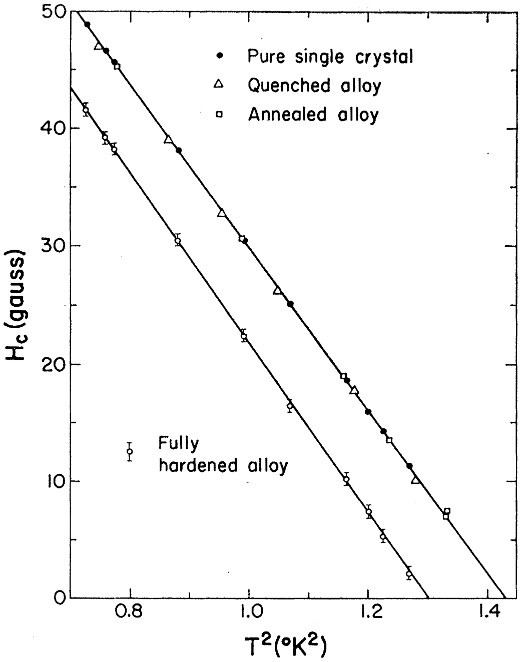


FIG. 11. Critical fields of pure Al and the Al-Mg-Si alloy after various heat treatments. Temperature values have been corrected on the basis of data on pure Al in reference 5.

TABLE I. Numerical results for fully hardened alloy.[a]

H_c (pure Al)	H_c' (hard alloy)	G	S
11.24	2.11	0.02	1.10
14.25	5.26	0.07	1.22
15.97	7.43	0.10	0.86
18.57	10.11	0.14	1.15
18.57	10.19	0.14	1.06
25.12	16.71	0.24	1.21
30.46	22.39	0.33	1.02
38.14	30.50	0.45	0.97
38.14	30.56	0.45	0.96
45.60	38.22	0.57	1.03
46.58	39.22	0.58	0.96
48.78	41.54	0.62	0.76

[a] All tabulated values are in gauss. See Fig. 10 for definitions of G and S.

defined to lie at the midpoint of the interval marked S as shown in Fig. 10.

Numerical values for all the transitions observed in the fully hardened condition are collected in Table I. Since the measurements of the carbon resistance thermometer used in this work are somewhat questionable, only the critical field values of pure Al are given as an indication of the temperature. It will be noted that the values of S remain substantially constant over the full range of measurement. This shows that the observed breadth can be regarded as the sum of the geometrical broadening, G (which increases linearly with H_0) and the fixed breadth characteristic of the hardened alloy and thus provides some justification for the present method of calculation.

Values of H_c' for the fully hardened alloy are plotted against T^2 in Fig. 11 together with points observed for the quenched and annealed alloy and the pure Al single crystal. Since the critical field of Al is indistinguishable from a parabolic temperature dependence in the present range of observation, the data are adequately represented by a straight line. It is apparent that the alloy shows reasonably good agreement with the critical field of pure Al in the quenched and annealed conditions. The displacement in H_c caused by precipitation hardening is substantial, corresponding to a decrease of about 0.05°K in T_c.

The linear dependence of H_c' upon T^2 displayed in Fig. 11 implies that both the alloy and pure Al follow the relation

$$H_c(T)=H_0[1-(T/T_c)^2], \tag{1}$$

differing only in the values of the constants, H_0 and T_c. Correcting the present measurements according to our most accurate determination of H_c for pure Al,[5] we obtain:

Fully hardened alloy: $H_0'=94$ gauss, $T_c'=1.140$°K

Pure Al single crystal: $H_0=99$ gauss, $T_c=1.196$°K.

It is readily verified that these constants satisfy the relation

$$H_0/T_c \simeq H_0'/T_c' \tag{2}$$

within the accuracy of the present measurements.

The present measurements do not extend over a sufficient fraction of the superconducting temperature range to justify a full-fledged thermodynamic analysis based on the validity of (2). However, the good description which (2) provides within the limited range of observation gives a strong clue regarding the probable physical origin of the observed shift. Within the accuracy of the present work, Eq. (2) is the type of critical field shift to be expected if a pure Al specimen were subjected to hydrostatic pressure.[12] This suggestion is developed in some detail in the discussion of the next section.

If the H_0 values were the true critical field intercepts at 0°K, the validity of (2) would further imply that γ (the temperature coefficient of the normal electronic specific heat) is unchanged by the precipitation hardening process. However, it is now known[13] from various recent measurements on Al that the critical field curve of this element must fall below the "parabolic law" [i.e., Eq. (1)] when the correct value of H_0 is used. The values of H_0 from the present measurements are probably about 10% smaller than the true values and thus

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[12] Both theory and experiment make it seem unlikely that Eq. (2) could ever hold exactly in the pressure effect. However, the probable deviations from Eq. (2) are within the experimental error of the present work. For a recent discussion see M. Garfinkel and D. E. Mapother, Phys. Rev. **122**, 459 (1961).

[13] N. E. Phillips, Phys. Rev. **114**, 676 (1959); M. A. Biondi and M. P. Garfunkel, *ibid.* **116**, 853 (1959). Deviation of the expected kind has recently been described by D. Gross and J. L. Olsen, Cryogenics **1**, 91 (1960).

no reliable conclusions about γ may be reached on the basis of these results.[14]

V. DISCUSSION

We interpret the present experimental evidence to show that the precipitation hardening process transforms these alloy specimens between two states, each of which, in terms of superconducting properties at least, satisfies the requirements of an equilibrium thermodynamic phase. These states correspond to the quenched and fully hardened conditions of the alloy, the quenched state closely approximating the properties of pure Al. It is significant that the full range of observed variation occurs at fixed chemical composition and seems solely a consequence of the thermal history of the specimen. From this fact it must be concluded that the *mode of dispersal* of the alloying elements is the dominant consideration.

The conditions of intermediate hardness (corresponding to underaging or overaging) exhibit irreversibility in the superconducting transition which reflects inhomogeneity in the superconducting properties of the alloy. From the observed magnetic behavior in such hysteretic transitions it is possible to draw some conclusions regarding the metallurgical transformations which attend the hardening process.

A. Superconducting Phenomenology

It seems most probable that the mechanism responsible for the observed magnetic hysteresis is the occurrence of persistent currents in a multiply-connected superconducting mesh within the volume of the alloy. Such behavior has been discussed in the literature.[1] A model which adequately describes the essential situation in these Al alloys was proposed many years ago by Mendelssohn.[15] As the hardness of the specimen increases from the quenched to the fully hardened condition, the sequential development of the hysteresis patterns indicates that the volume of the alloy consists substantially of two pseudo-phases. The pseudo-phases differ in superconducting properties and correspond approximately to the better defined states observed in the quenched and fully hardened conditions. For brevity we shall term these two pseudo-phases the q and h phases, where q phase denotes the material whose superconducting properties are substantially equivalent to that of the quenched alloy (or pure Al) and the h phase refers to the material whose properties ultimately permeate the entire alloy volume in the fully hardened condition. In terms of the experimental hysteresis observations, the q phase governs the course of the permeability plot in the S–N transition in the early stages of hardening, while the h phase is responsible for the drop below the knee in the return N–S transition (for example, near -6 gauss in Fig. 5).

We designate the h and q phases as pseudo-phases since it is unlikely that they possess well-defined boundary surfaces, nor is it likely that they have really homogeneous superconducting properties.[16] It is quite certain that these regions do not constitute thermodynamic phases in the sense that the term is employed in metallurgy. Despite these uncertainties, the hysteresis curves indicate that a separation into two multiply-connected regions with distinct superconducting properties is a reasonable working model for discussion. Metallurgical evidence to be cited later supports this view and also explains why one could scarcely expect a more sharply defined situation than is observed here.

It will be noted that H_c for the h phase decreases appreciably as hardening proceeds. (An increase in H_c for the q phase also seems to occur in the early stages of hardening.) The height on the permeability plot at which the knee occurs in the N–S transition provides an approximate estimate of the fraction of the alloy volume which is in the h phase.

In terms of our model the evolution of the hysteresis patterns represents the growth of the h phase within the specimen during the early stages of precipitation. So long as both q and h phases are present, the hysteresis loop is observed. This indicates that both the h and q phases exist within the specimen volume in the form of multiply-connected networks.[17] For an aging time somewhere between 8.5 and 11 hr (at 175°C), the q phase is squeezed out and the subsequent behavior is governed by the h phase up to the condition of maximum hardness.

B. Metallurgical Aspects

It is well established that the changes in mechanical properties of a precipitation hardening alloy result from the development of solute-rich regions within the lattice of the solvent metal.[18] X-ray scattering studies of Al-Mg-Si indicate that the Guinier–Preston (G. P.) zones in this alloy are in the shape of needles oriented in $\langle 100\rangle$ directions in the Al matrix which grow in length in the initial phase of aging.[19] With continued aging, the one-dimensional growth is followed by a two-dimensional or platelet stage of development, and, finally, by a three-dimensional growth from which a true precipitate phase (Mg_2Si) emerges. Particle size estimates indicate that the maximum dimensions are about 100 A in both the needle and platelet stages of growth.

Geisler and Hill have reported the correlation be-

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[14] Recent calorimetric measurements by F. A. Otter (to be published) give the result that the hardening process produces an increase of about 1% in γ in the present alloy.

[15] K. Mendelssohn, Proc. Roy. Soc. (London) **A152**, 34 (1935).

[16] The residual transition broadening observed in both the annealed and fully hardened conditions is evidence that our pseudo-phases are not rigorously homogeneous.

[17] R. W. Shaw and D. E. Mapother, Phys. Rev. **118**, 1474 (1960); also reference 15.

[18] A. Guinier, *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1959), Vol. 9, p. 294.

[19] A. H. Geisler and J. K. Hill, Acta Cryst. **1**, 238 (1948); also A. H. Geisler, *Phase Transformations in Solids* (John Wiley & Sons, Inc., New York, 1951), p. 387.

tween x-ray determination of particle size (and shape) with the time and temperature of the aging treatment.[19] From these results we conclude that, under the conditions of the present work, the development of full hardness and maximum shift in critical field occurs during the needle-like stage of G.P. zone growth. Indeed, the growth appears to be predominantly one-dimensional at the aging temperature of the present work for times far exceeding that required for maximum hardness since Geisler reports preponderantly one-dimensional clusters in this alloy when aged for 30 days at 200°C.

The average dispersion of the G.P. zones in Al-Mg-Si can be calculated from the known concentrations of Mg and Si using an estimated value of 200 as the average number of atoms in a single zone. This gives a density of 3×10^{18} zones/cm^3 or an average center-to-center spacing of 10^{-6} cm (i.e., about equal to the zone length) and is of the same order of magnitude as experimentally determined densities for similar precipitation hardening alloy systems which have been studied in greater detail than Al-Mg-Si. In view of the close proximity of the G.P. zones, it is reasonable to suppose that the coherency strain fields overlap in the condition of maximum hardness. While direct observation of the strain fields around G.P. zones in Al-Mg-Si has not been reported, such observations have recently been described by Nicholson and Nutting using electron microscopy on thin foils of Al-Cu.[20] Substantial overlap of the strain fields seems evident in their photographs and presumably this condition also occurs in bulk material.

Further inferences regarding the probable mode of growth of the G. P. zones follows from the recent work of Livingston and Becker.[21] These investigators have applied magnetic measurements to a Cu–Co alloy to determine the size and spacing of the clusters of Co atoms which form during the aging process. They find that the individual particle size increases in close correlation with the increase in mechanical hardness but in such a way as to maintain the total volume of the precipitating aggregates constant. Thus the dimensional growth of individual particles occurs at the expense of the number of particles, a mode of evolution predicted theoretically by Greenwood[22] and commonly observed in the spheroidization process in steels and other age-hardening alloys.

C. Physical Interpretation of Superconducting Changes

The basic problem of interpretation is that of establishing the physical identity of the h and q phases in the present alloy. In view of the foregoing metallurgical picture of the hardening process, we think it reasonable to identify the h phase with the overlapping strain fields around the G. P. zones while the q phase corresponds to the unstrained regions in the Al matrix.

It is recognized that the stress near a G. P. zone must vary substantially on a microscopic scale (say, 10^{-7} cm) but we assume that the coherence characteristic of the superconducting state enables the superconducting electrons to average over the most extreme local variations. Pippard's range of coherence parameter ξ_0 has a value near 10^{-4} cm for pure Al, and his line of argument indicates a considerably reduced value of ξ_0 for such an impure alloy as the present one.[23] However, the situation is not quantitatively well defined at present so that no reliable value can be given for the characteristic distance over which the averaging occurs. (We would guess the averaging dimension to lie somewhere between 10^{-5} and 10^{-6} cm.)

Our hypothesis regarding the identity of the h phase can be tested by calculating the average stress within the alloy in the condition of maximum hardness. Values of $((\partial H_c/\partial P)_{T_c}$ have been determined for Al which permit at least an order-of-magnitude estimate.[24,25] From the shift ($\Delta H_c = -9$ gauss) observed near T_c at maximum hardness, an average stress between 27 and 40×10^3 psi is obtained [depending on the value of $(\partial H_c/\partial P)_{T_c}$]. From Fig. 1 it is seen that this value is of the order of magnitude of the yield strength of the alloy, as seems appropriate and reasonable in view of the averaging effect of the superconducting electrons. Qualitatively, this interpretation also makes the unequivocal prediction that the average stress in the Al matrix around the G. P. zones is *compressive.* This result depends on the nature of the misfit between the Al lattice and the atomic clusters in the G. P. zones which, so far as we can determine, is not well understood at present.[26]

An independent argument favoring the strain field hypothesis is the following. All experimental evidence regarding the precipitation process shows the size and dispersion of G. P. zones to be much finer in the initial stage of hardening than that prevailing at maximum hardness. This means that in the initial stage of hardening both the size and spacing of the G. P. zones will be considerably smaller than the penetration depth, λ. (For pure Al, $\lambda\simeq5\times10^{-6}$ cm.[23]) Without laboring the question of whether the clusters of Mg and Si atoms are themselves superconducting, isolated regions of this size would show a very steep critical field curve owing to the well-known thermodynamic consequence of

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[20] R. B. Nicholson and J. Nutting, Phil. Mag. **3**, 531 (1958).

[21] J. D. Livingston and J. J. Becker, Trans. Am. Inst. Mining Met. Engrs. **212**, 316 (1958); J. D. Livingston, Trans. Am. Inst. Mining Met. Engrs. **215**, 566 (1959).

[22] G. W. Greenwood, Acta Met. **4**, 243 (1956).

[23] T. E. Faber and A. B. Pippard, Proc. Roy. Soc. (London) **A231**, 336 (1955); also *Progress in Low-Temperature Physics* (Interscience Publishers, Inc., New York, 1955), Vol. I, p. 159.

[24] N. L. Muench, Phys. Rev. **99**, 1814 (1955).

[25] D. Gross and J. L. Olsen, Cryogenics **1**, 91 (1960).

[26] H. K. Hardy and T. J. Heal, *Progress in Metal Physics* (Interscience Publishers, Inc., New York, 1954), Vol. 5, pp. 212–213.

dimensions smaller than λ.[27] However, the experiments clearly show the h phase to develop in the early stages of hardening and to have an H_c less than the rather small H_c values of pure Al over the entire temperature range of measurement.

We conclude that the size of the G. P. zones, as estimated from the number of Mg and Si atoms is far too small to affect the superconducting properties in the way observed here and that what we have termed the h phase is the combined effect of many overlapping "zones of influence" (presumably, the stress fields) which extend for much larger distances. It should be further remarked that the assumption of complete homogeneity in size and dispersal of the G. P. zones (and their associated stress fields) leads to difficulties in understanding the survival of the q phase in the early stages of hardening. If the alloy were really homogeneous on a scale of 10^{-6} cm, we would expect the averaging capabilities of the superconducting electrons to yield a single H_c which would presumably decrease continuously from the quenched to the fully hardened condition. Such a process is manifestly in disagreement with the experimental facts which show a homogeneous and well-defined H_c only in the quenched and fully hardened states.

From these considerations it seems that the hysteresis characteristic of the underaged condition arises from a microscopic inhomogeneity in the alloy which occurs on a dimensional scale somewhat larger than the coherence length of the superconducting electrons. Since other evidence indicates precipitate growth to occur by the aggregation of small atomic clusters to form larger ones, we propose that inhomogeneity on the scale necessary to produce the macroscopic superconducting changes results from the clustering of G. P. zones with the consequent overlap of their associated stress fields. The phenomenological arguments of Sec. A indicate that the value of μ_e at the knee of the N–S transition gives the fraction of the alloy volume influenced by the coherence stress, while the shift in H_c gives an approximate estimate of the average stress. The variation with aging time of the fractional volume of the h phase and the critical field shift are shown in Fig. 12.

The effects associated with overaging were not studied in much detail, but it is clear from Fig. 8 that the character of the hysteresis in the overaged condition shows significant departures from the behavior seen in the underaged states. Generally speaking, the changes in the hysteresis pattern suggest that inhomogeneity in the alloy occurs on a larger dimensional scale than was true in the underaged condition. At least three associated metallurgical effects would contribute to this situation:

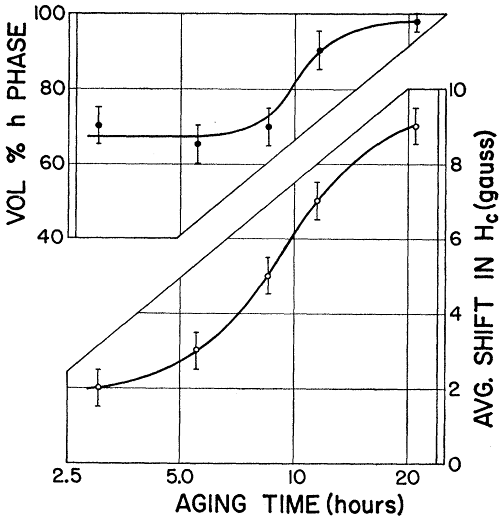

FIG. 12. Variation in volume and average critical field of the h phase with aging time. Both curves are derived from the data of Fig. 9 according to the interpretation described in the text.

(a) With continued aging an equilibrium precipitate phase appears of a size readily resolvable by optical microscopy.

(b) Depletion of solute from the matrix creates regions of relatively pure Al.

(c) Registry between the lattice and the clustering solute atoms breaks down with a consequent relaxation of coherency stress.

We would expect this relaxation process to involve intermediate stages in which the microscopically interlaced stress fields of the G. P. zones give way to the longer range stress inhomogeneity characteristic of mechanical inclusions in the Al matrix (i.e., the newly emergent equilibrium precipitate phase).

The influence of these effects is to be seen in the hysteresis pattern after 100 hr of aging (Fig. 8). Relaxation of coherency stress is indicated by the reduction in ΔH_c at the start of the S–N transition (as compared with its value at maximum hardness). Disregarding for the moment the sharp initial steps in the S–N and N–S transitions, the data now indicate a wide spectrum of H_c values within the alloy. While this is clearly different from the behavior in the underaged states, such broad transitions are well known to be characteristic in cases where strain is inhomogeneous on a scale comparable to a specimen's dimensions and also in inhomogeneously prepared alloys.

The sharp drop in μ_e in the N–S transition is very similar to the supercooling observed in pure metals. Since Al is outstanding for its tendency to supercool, this suggests that the Al matrix, now depleted of Mg

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[27] D. Shoenberg, *Superconductivity* (Cambridge University Press, New York, 1952), 2nd ed., pp. 166–174. A spectacular recent example of the effect of size on H_c is given by G. M. Androes and W. D. Knight, Phys. Rev. **121**, 779 (1961), who report $H_0 > 25$ kgauss for tin specimens 40 A in thickness. However, it must be admitted that the h phase on our alloy, being embedded in the q phase of rather similar chemical and superconducting properties, is in a rather different situation from finely divided superconducting particles in an insulating matrix.

and Si and relieved of some of the coherency stress, is beginning to behave like ordinary Al. The difficulty with this interpretation is that the S–N transition indicates that very little of the specimen volume is unstrained. Moreover, such unstrained Al as is present must be located in disconnected regions since if it provided a continuous path for persistent currents they would shield the strained regions from the magnetic field and produce a sharp S–N transition near the H_c of pure Al (as actually occurs in the early underaged conditions). It may be true that the supercooling can occur in the pure Al regions when the stress gradients are reduced and this would explain the observed results.[28]

The abrupt increase in μ_e in the S–N transitions of Fig. 8 presents another problem in detailed interpretation. The rise must represent a relaxation of a nonequilibrium state since it is too sharp to be reconciled with either the demagnetizing factor of the specimen or the other evidence, both metallurgical and superconducting, that the stress (and therefore the H_c value) is grossly inhomogeneous. The effect is phenomenologically identical with that observed in the S–N transitions of Fig. 4 except that the rise occurs at a field characteristic of the strained Al and affects a smaller fraction of the specimen volume.

We conclude that the major evolutionary stages in the magnetic transitions (with increasing aging time) result from the growth and subsequent regression of regions of local strain in the Al matrix. The regions of strain are associated with the G. P. zones and they alter the superconducting behavior by producing local distortion in the Al lattice. The fundamental effect is presumed to be similar to that observed in the well-known pressure effect. The superconducting properties of the alloy return to those of pure Al as overaging proceeds, since prolonged heating causes loss of registry between the Al lattice and the clusters of precipitating atoms, with a consequent reduction of internal strain.

D. Comparison with the Pressure Effect

If our hypothesis is correct in attributing the observed shift in H_c to stress induced in the precipitation process one would expect some similarity between the present results and those produced by externally applied pressure. Unfortunately, the search for similarities is complicated by the fact that the internal consistency of the available pressure results is poor. All published results for Al thus far have been obtained by the ice bomb technique[29] and, while precision of 10% is usually claimed, the variation between the reported pressure derivatives suggests that the uncertainty in pressure is more like 50%.

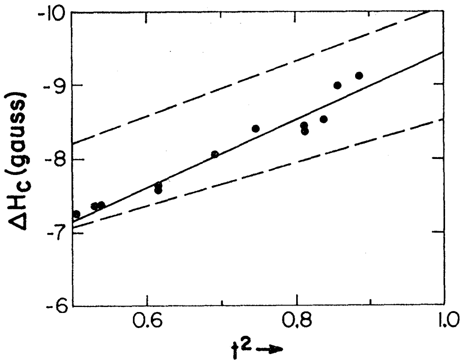

FIG. 13. Comparison of the temperature dependence of the critical-field shift of fully hardened Al-Mg-Si with the shift expected in pure Al under a hydrostatic pressure of 1910 atm. The solid line gives a least-squares fit to the experimental points observed for the Al-Mg-Si alloy. The dashed lines represent the upper and lower limits of accuracy set by the measurements of Gross and Olsen (reference 25).

The recent work of Gross and Olsen[25] provides an estimate of the relative magnitudes of the pressure derivatives of H_c for Al at T_c and 0°K [i.e., $(\partial H_c/\partial p)_{T_c}$ and (dH_0/dp)]. Defining the ratio

$$A=(\partial H_c/\partial p)_{T_c}/(dH_0/dp),$$

Gross and Olsen report values equivalent to $A=1.55\pm0.2$. Assuming the present hardening effect to be equivalent to a constant internal pressure, the value $A\simeq1.9$ is obtained over the limited temperature range of these measurements. The values of A provide a reasonable basis for comparison in view of the considerable uncertainty in pressure since present experimental work indicates that $(\partial H_c/\partial p)_T$ is substantially pressure independent for pressures less than 3000 atm.[30] A graphical comparison is presented in Fig. 13 where (by assuming a pressure of[31] 1910 atm) the results of Gross and Olsen are matched to the maximum H_c of the alloy [at $(T/T_c)^2=0.916$]. The dashed lines give the reported upper and lower limits of the measurements of Gross and Olsen.

The significance of the greater slope shown by the hardened alloy in Fig. 13 is difficult to assess in view of the experimental uncertainty. The A value for the hardened alloy is in closer agreement with Gross and Olsen than is a previous result obtained by Olsen using the same method which gives[32] $A=0.35$ (i.e., a slope reversed from that shown in Fig. 13). The difference between the two ice bomb determinations of A is now attributed to error in the pressure.[25] It is not explained how an error in the pressure can produce such a drastic change in A, a quantity which, at these pressures, is expected to be constant.

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[28] It should be noted that no trace of supercooling occurs in any of the heat treatments from the quenched to the fully hardened condition.

[29] C. A. Swenson in *Solid-State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1960), Vol. II, p. 62.

[30] L. D. Jennings and C. A. Swenson, Phys. Rev. **112**, 31 (1958).

[31] The corresponding internal pressure estimated on the basis of Muench's results (reference 24) is 2800 atm.

[32] J. L. Olsen, Helv. Phys. Acta **32**, 310 (1959).

We can only conclude that matters are somewhat confused at present in the pressure effect on Al. To the extent that any comparison has meaning, there appears to be a qualitative similarity between the present hardening effect and the effect of hydrostatic pressure.

E. Impurity Effects

Throughout the foregoing discussion it has been assumed that the state of agglomeration of the Mg and Si in the alloy has been responsible for the observed changes in superconducting behavior. This is in accord with the observations since the full variety of effects can be seen with a single specimen simply by varying the thermal history.

Recently Chanin *et al.*[33] have described the effect on T_c of Al which accompanies the addition of dilute amounts of various elements including Mg and Si. At concentrations of Mg comparable to the amount present in our alloy there is a displacement in H_c similar in both direction and magnitude to that observed here. Addition of Si has a somewhat different effect since, after an initial decrease, T_c appears to rise with increasing Si content. In view of these results it is interesting that our Al-Mg-Si alloy, which is very impure by their standards, shows such good agreement with pure Al in the quenched condition.

The following possibilities occur for reconciling the apparent disagreement between these results. It may happen that the chemical natures of Mg and Si are such that their joint presence results in the cancellation of their individual effects. Suggestion of this is seen in the somewhat different effects caused by these two elements in the work of Chanin *et al.*[33] The mutual preoccupation of Mg and Si in the sharing of chemical bonds is also demonstrated by the formation of a molecular precipitate of Mg_2Si. Against this possibility is the fact that our alloy also contains measurable quantities of Fe, Cu, and traces of three other elements which collectively appear to have no perceptible effect on T_c.

An alternative possibility is that some clustering of solute atoms may occur in the dilute binary alloys with results similar to those observed in Al-Mg-Si. The reported details of Chanin *et al.* are not sufficient to permit an appraisal of this point. However, it could be checked by varying the heat treatment of the dilute alloy specimens.

A final possibility is suggested by the much larger resistance ratio of the present alloy in comparison with the dilute alloys of Chanin *et al.* As noted in Sec. III-B, the Al-Mg-Si alloy has, at all stages of hardening, a value of ρ about twice the maximum reported in the dilute alloy work.[33] It has been proposed[34] that there may be two different regimes in a superconducting alloy depending on whether the normal electronic mean free path, l, is greater or less than ξ_0, the coherence length of the pure material. Comparison with the dilute alloy results indicates that our Al-Mg-Si specimens must lie well into the "dirty superconductor" regime characterized by l values less than ξ_0. Pippard and Faber[23] have argued that under these circumstances the effective range of coherence in the alloy may be reduced to values less than the penetration depth λ, a situation leading to the occurrence of a negative surface energy at the boundary between the superconducting and normal phases. While we see no clear manifestation of a negative interphase energy in the present results, it would seem that the conditions postulated for its occurrence imply a capability of the superconducting electrons to respond to much more localized variations in the metallic lattice. Such behavior is in agreement with the present observations. According to this interpretation the results of Chanin *et al.* differ from the properties of Al-Mg-Si because they apply principally to the region where $l \geq \xi_0$.

As a concluding observation we wish to point out that, in our opinion, the present work shows that there is merit in making magnetic measurements of both the S–N and N–S transitions—especially in work on alloys. Complicated as the present results may seem, they are not nearly as strange as the picture which emerges when only the S–N transitions are considered. While we do not assert that the interpretation given here is necessarily the ultimate truth, the development of a reasonably self-consistent explanation has been greatly aided by the information contained in the full hysteresis pattern.

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We are indebted to many colleagues for discussions and comments which have been helpful in crystallizing our ideas, especially concerning the metallurgical aspects of this problem. In particular, we wish to mention the assistance and encouragement provided by J. S. Koehler in the early stages of the work, and recent valuable critical comments of J. B. Newkirk concerning the lore of precipitation hardening. The experimental work was aided substantially by the efforts and advice of B. S. Chandrasekhar, J. F. Cochran, and T. S. Noggle. One author (D. E. M.) is pleased to acknowledge the support of the J. S. Guggenheim Foundation and the cordial hospitality of the Physics Department of Cornell University during the final preparation of this manuscript.

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[33] G. Chanin, E. A. Lynton, and B. Serin, Phys. Rev. **114**, 719 (1959). Also see D. P. Seraphim, C. Chiou, and D. J. Quinn, J. Appl. Phys. (to be published).

[34] P. W. Anderson, J. Phys. Chem. Solids **11**, 26 (1959).