FINAL REPORT

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HIGH TEMPERATURE ANNEALS OF
DEFECTS QUENCHED IN METALS

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The results achieved under this research contract will be discussed in the order listed in the Proposed Technical Program of the most recent Research Proposal.

A. High Temperature Anneals

and E. High Temperature Pulsing in Cryogenic Liquids.

Numerous studies had shown that the early interpretation of defect annealing in gold in terms of single vacancies migrating to a fixed number of sinks was a gross oversimplification. Multiple-vacancy interactions complicated the interpretation of the results. Conflicting reports of the divacancy binding energy were in print. Because of the DC measuring techniques involved, all anneals had been made at relatively low temperatures, e.g. $<100^{\circ}\text{C}$. The measured activation energies were some sort of average over the defects present in the quenched materials. An appreciable increase in annealing temperature would have annealed out the excess resistance too rapidly for accurate measurements to be made by the existing technique. In that method, the specimen was held in a liquid nitrogen bath, then transferred rapidly to a bath at the desired annealing temperature for a given time interval and then returned to the nitrogen bath. Annealing times shorter than a few seconds could not be made accurately.

This project carried out anneals at significantly higher temperatures than had been done previously. Isothermal anneals at temperatures up to about 400°C for intervals of tens of

milliseconds were made by means of an electronic control device. Effective migration energies determined by this technique turned out to be in the same range as those observed in low temperature anneals. It was concluded that the binding energy of divacancies in gold was high, i.e. $\geq 0.35\text{eV}$. Because of this, higher annealing temperatures would have been required to observe a significantly different annealing behavior.

Numerous techniques were devised to increase the maximum annealing temperature, but none were successful. Mineral and silicone oils and, indeed, every liquid tried, vaporized irregularly along the length of the specimen. The sudden loss of thermal contact in these regions caused the specimen to heat locally to beyond the melting point. Liquid helium pumped to below its λ -point was the most promising specimen environment. However, very large electric currents were required to Joule heat the specimen since its residual resistance was so low. Large mechanical vibrations of the specimen were observed, presumably from magnetic interactions.

Since Wang, Seidman and Balluffi¹ had simultaneously and independently performed high temperature anneals by a different technique and come to similar conclusions as ours, no further attempts were made to determine a specimen shape and specimen environment which would permit higher annealing temperatures.

During this portion of the research, however, an electronic feedback temperature controller was developed. Almost all other quenching experiments have had no means of reproducing quench

temperatures or quench rates. At the specimen temperatures required in most quenching experiments, the specimen temperature varies quite rapidly with specimen current. Thus, when a rheostat is used to control current (and hence temperature), it is rather difficult to return to the same quench temperature. Experiments requiring quenches from a fixed temperature had to be analyzed by using a correction factor based on an often imprecisely known formation energy. The circuit developed under this contract employs a sensing bridge, the output of which is used to bias a power transistor which controls the specimen current. The bridge balance is quite sensitive and reproducible, so that precise, repeatable anneal, or quench, temperatures can be set. Another feature of the controller is that the bridge balance can be adjusted electronically. By applying an analog signal, the specimen temperature can be made to follow any functional form which does not require heating or cooling rates in excess of those determined by the power supply and specimen environment. This controller made possible the portion G of this research program.

This portion of the work was reported at the APS March Meeting Bull. Am. Phys. Soc. 12, 389 (1967) R. M. Emrick, High Temperature Anneals of Defects Quenched in Gold and was published as "Pulse Annealing of Gold," R. M. Emrick, Phys. Letters 25A, 249 (1967). The temperature controller is described in "Programmable Temperature Controller for Small Diameter Wires," R. M. Emrick and D. E. McDonald, Rev. Sci. Inst. 40, 82 (1969).

B. Pressure Effect on the Anneal of Quenched-In Resistance in Aluminum

Two measurements^{2,3} of the activation volume for self-diffusion and one of formation volume⁴ in aluminum yielded values in excess of an atomic volume. No other fcc metal measured to date had shown such high volumes. We therefore attempted to measure both the formation and motional volume of aluminum independently. In this portion of the project, the pressure effect on the annealing rate of excess electrical resistance quenched into aluminum from two different temperatures was studied.

As in gold, divacancies in aluminum complicate the annealing behavior. However, by quenching from a high temperature (580°C) so that the vacancy concentration was high and a large number of divacancies could form during quench and annealing at temperatures below -60°C where vacancies are immobile, a divacancy motional volume was inferred. The slope ratio method gave a divacancy formation volume of (0.17 ± 0.02) atomic volumes.

Low temperature quenches (331°C) reduce the number of divacancies which can form during quench. However, those which do form are so mobile that even though few in number, they can make an appreciable contribution to the annealing at temperatures where single vacancies are mobile. In this case, the anneals were carried out at 0°C at a series of pressures. The effective motional volume inferred from the slope ratio method was (0.18 ± 0.02) atomic volumes. This motional volume was

shown to be consistent with a single vacancy motional volume of the same value. This value is consistent with the .15 atomic volume value found earlier for gold.⁵ It was concluded that if a large activation volume for self-diffusion in aluminum was to be consistent with these results, a large divacancy concentration at high temperatures would be required. See G. below for further discussion. This work formed the thesis research of Brent J. Buescher. It was reported at APS March Meetings, Roy M. Emrick and Brent J. Buescher, Bull. Am. Phys. Soc. 11, 184 (1966) and Brent J. Buescher and Roy M. Emrick, Bull. Am. Phys. Soc. 13, 418 (1968). The complete description is contained in the thesis, Brent J. Buescher, "The Pressure Effect on Defect Migration in Aluminum" Thesis, University of Arizona, Tucson, Arizona, 1969. It was published as "Pressure Effect on Defect Migration in Aluminum," B. J. Buescher and Roy M. Emrick, Phys. Rev. B 1, 3922 (1970).

C. The Effect of Mechanical Strains on High Temperature Annealing.

No personnel were available to conduct this proposed research.

D. Deleted.

E. See under A.

F. Study of the Effect of Pressure on the Mössbauer Spectrum of ^{57}Co in NaCl .

The pressure effect on thermal rate processes allows one to use thermodynamic arguments to determine volume changes associated with the process, as in the case of the previously discussed quenching experiments. Such measurements are macroscopic averages over the entire distribution of defects. The

Mössbauer effect provides an atomic-scale probe to observe individual defects. When divalent impurities enter an alkali halide lattice substitutionally, charge neutrality requires that there be a vacant site on the same sub-lattice as the impurity. Thus, if Fe^{2+} enters a sodium ion lattice site, an adjacent sodium ion site should also be vacant.

If, under the application of pressure, there is a relaxation of the vacancies' neighbors toward it, the change in symmetry of the environment of the ^{57}Fe should result in a quadrupole splitting of the Mössbauer spectrum. Numerous NaCl specimens were prepared with the appropriate cobalt isotope. Several types of spectra were observed, indicating a number of possibilities. One is that the iron has precipitated as FeCl_2 , another range of possibilities is that the iron is in charge states from +1 to +3. A recent review article by Murin and Seregin⁶ lists the range of possibilities and the evidence to support them. The present work adds another bit of conflicting evidence to the list.

In particular, Murin and Seregin list three types of spectra observed in cobalt-iron- and tin-doped alkali and silver halides:

Type 1 - a wide doublet (splitting $\approx -1.2\text{mm/s}$) with isomer shift characteristic of Fe^{2+} ($\approx -1.2\text{mm/s}$). This is very similar to the spectrum produced by CoCl_2 .

Type 2 - a narrow doublet with a smaller isomer shift, characteristic of Fe^{3+} (splitting and shift roughly half those of type 1). Found in several alkali halides and AgCl , especially with lower concentrations of impurity ^{57}Co .

Type 3 - a broad singlet with isomer shift characteristic of Fe^{2+} (i.e. about the same as type 1). Found in AgCl (usually at higher impurity concentrations) but not in alkali halides. Below 240°K in AgCl , the single line splits into a doublet.

Type 4 - a singlet with large isomer shift ($\approx -2.1\text{mm/s}$), indicative of Fe^{1+} . Found only in combination with type 2 (in varying proportions, depending on sample preparation and treatment), though type 2 has been observed without type 4.

The principal interpretations for the spectra are as follows.

Type 1 seems fairly definitely to result from CoCl_2 precipitated into microcrystals. Type 2 is thought to be substitutional Fe^{n+} (n probably 3) with a charge compensating vacancy neighboring it thus causing a quadrupole splitting. Others suggest the "doublet" is independent $2+$ and $3+$ singlets, although other experiments rule this out. A third possibility is that the doublet results from a complex with another impurity (e.g. $\text{Fe}^{3+} + \text{O}$, etc.). Type 3 may be either Fe^{2+} with the charge associated vacancy moving rapidly enough to make the average field nearly cubic (i.e. broad singlet rather than resolved doublet) or a divalent interstitial with two cation vacancies. Type 4 is thought by some to be Fe^{1+} either substitutional, interstitial or complexed.

In the present experiment most of the spectra were poorly resolved examples of Type 1 (CoCl_2). Sometimes type 3 was mixed with type 1 (although it may have been weakly present in all cases. Despite a variety of preparation techniques, which included those used by previous investigators, type 4 could not

at all be reproduced and only one spectrum that might have been type 2 was seen. A wide range of Co^{57} concentrations and diffusion times were used, all with the same results.

Spectral types could be changed reproducibly by annealing in various atmospheres such as H_2 , Cl_2 or HCl . The spectra were altered slightly by the various atmospheres. However, H_2 altered the spectrum drastically. A clearly resolved line appeared at $+3.1$ mm/sec. It appears to be unrelated to any other lines seen in Mössbauer studies of alkali or silver halides.

Several vapor-deposited specimens were sectioned by standard diffusion measurement techniques. (Specimens prepared by dropping the $\text{Co}^{57}\text{Cl}_2$ in solution on to the crystal had concave faces and were unsuitable for such measurements. However, as mentioned earlier, observed spectra were independent of preparation techniques.) The penetration profiles, for 15-20 25μ microtome cuts, showed that the Co^{57} had penetrated deeply into the NaCl crystals. Minimal precautions were taken to prevent evaporation of the CoCl_2 from the crystal face, so the concentration of activity first increased, then decreased with depth, precluding a test of bulk vs. grain boundary diffusion. Samples have been sent out for spectrographic analysis, but the results have not yet been received.

Several runs were made at pressures up to 8 kbar. No significant changes in the quadruple splitting were observed (although some may be revealed by the computer analysis) on types 1 and 3, as would be expected if there were no charge-associated vacancies.

This is the first report of a type 3 spectrum in NaCl. Previously it was observed only in AgCl. The type 3 singlet was stronger than the doublet (although the doublet was usually quite weak) and the singlet did not split into a doublet at temperatures as low as 200°K.

This research forms the thesis project of Carl N. Helmick, Jr. Last summer, he felt it necessary to leave in order to fulfill a job commitment to the Office of Naval Research. It was therefore impossible to bring this portion of the project to completion before the expiration date. The laboratory work is essentially complete. Mr. Helmick is in the process of modifying his program for use on the computer at China Lake (his present location). He is still enrolled as a graduate student and intends to analyze and write up his results both for a Ph.D. thesis and journal publication. At that time copies of the publication will be forwarded to the AEC.

G. The Effects of Pressure and of Quench Rate on Quenched-In Resistance.

Quenching experiments are frequently used to infer equilibrium properties of defects at the temperature before quench. Since the defects are mobile, some of them will be able to reach sinks (surfaces, grain-boundaries, dislocations) during the quench. The number lost will be a function of the quench rate. In addition, those not reaching sinks may combine with other defects, so that the single-to di- ratio after quench may differ dramatically after quench from the pre-quench temperature equilibrium ratio.

A number of theoretical calculations of the fractional-loss during quench had been made. All of them assumed that the temperature decreased linearly with time during quench. The few experimental results available relied on cooling rates provided by varying specimen environments. Many were exponential rather than linear, and the range of available rates depended on the range of available quench media.

In this portion of the experiment, the programmable temperature controller described in A was driven by a linear voltage ramp so that the specimen temperature could be reduced linearly from a predetermined quench temperature. Gold and aluminum specimens of 5-9's purity and .003 in. diameter were mounted in a pressure vessel. High purity argon at pressures of $\frac{1}{2}$, 2, 4 and 6 kbar was the pressure medium. After an initial cleansing anneal in the atmosphere, the specimens were mounted in the pressure vessel where they remained for the entire experiment. The specimen was heated to the quench temperature after the system had been pumped to the desired pressure. A linear quench was then made and the resistance of the specimen compared with that of an unquenched dummy by standard bridge techniques. The measurement was made at ambient temperature for gold ($\sim 23^{\circ}\text{C}$) since negligible annealing occurs under these conditions (and at a reference pressure of about 1400 psi). For aluminum, the pressure vessel was packed in dry ice to prevent post-quench annealing since in aluminum, vacancies and divacancies are quite mobile even at 0°C . In both cases a cleansing anneal was then made, the specimen resistance was again measured and another quench-cycle repeated.

By means of linear extrapolations to infinite quench rates, equilibrium vacancy concentrations were inferred. For gold, the value was $6.8 \pm 0.4 \text{ cm}^3/\text{mole}$ (0.67Ω) and for aluminum $6.38 \pm 0.15 \text{ cm}^3/\text{mole}$ (0.638Ω). When properly corrected, values for the formation volume determined by other methods and by other quenching experiments were found to be in good agreement with these values. When the motional volumes are added to these formation volumes, the results are in reasonable agreement with the activation volumes for self-diffusion, except for several results for aluminum. These latter values were much higher than the sum and were measured by less direct techniques such as pressure effect on creep. This may be an indication that the mechanisms are not entirely diffusion limited or that other errors are involved. In any event, aluminum does not appear to have defect volumes appreciably different from other fcc metals which have been studied.

The pressure effect on loss rate was slightly (factor of 2 or 3) in excess of that which would be expected from motional volumes of single vacancies only. The effect was small and scatter large, but the result was taken to indicate that a significant fraction of the defects were annealing to clusters. The scatter was also just enough to be unable to make meaningful comparisons with the various models for loss during quench. Several studies were therefore suggested. First, the technique should be tried on platinum, where defect clustering appears not to occur. Then, quenches should be made in doped and strained materials to determine experimentally the effects of the various sinks.

Before the end of the contract period, several measurements were made on 5 9's platinum. A rough value of $7 \pm 1 \text{ cm}^3/\text{mole}$ was determined for the formation volume. This value is also in the range observed for other fcc metals. Pressure effect on loss rate appeared to be smaller than for gold and aluminum, consistent with a dislocation sink mechanism. Taken together, the pressure quench and annealing results support the presumption that $\Delta V_F + \Delta V_M = \Delta V_{ACT}$. In the case of aluminum, they strongly suggest that the large activation volumes inferred from creep and other measurements are the result either of an inappropriate model or of experimental error. The increased precision of the vacancy parameters provides a better basis against which theoretical calculations can be checked. The feasibility of a loss-mechanism determination has been demonstrated.

The gold and aluminum results formed a portion of the thesis research of Patrick B. McArdle and was published as "Effect of Pressure on Quenched-In Electrical Resistance in Gold and Aluminum," R. M. Emrick and P. B. McArdle, Phys. Rev. 188, 1156 (1969). The platinum results were reported at the March APS meeting Bull. Am. Phys. Soc. 16, 406 (1971) paper FI 3 "Effect of Pressure on Equilibrium Vacancy Concentration in Platinum," R. M. Emrick.

H. Study of the Effect of Pressure on Ferroelectrics.

Both potassium nitrate and sodium nitrite show first-order, order-disorder transitions across the phase boundary between the low-temperature ferroelectric and the high-temperature non-ferroelectric regions. Compared with other order-disorder

ferroelectrics, their crystal structure is relatively simple. This portion of the research extended the two most direct methods of investigation (spontaneous polarization via hysteresis loops and dielectric measurements) into the high pressure regions.

It was found that KNO_3 -I exhibits a Curie-Weiss behavior in pressure with a well-defined pressure Curie constant $C^* = -276 \pm 3$ kbar and extrapolated Curie-Weiss pressure, $p_0 = 4.68 \pm 0.07$ kbar. At higher temperatures C^* became slightly more negative and p_0 increased. The peak values of the dielectric constant at the I-III boundary increase with pressure. These two results gave a value of dT_0/dp of $\approx 25^\circ\text{C/kbar}$.

In region III, the spontaneous polarization had maximum values well below those reported previously, but more consistent with those for related materials. (Virgin crystals were used for each crossing of the phase boundary into phase III. An anomalously high value was recorded for a crystal that was deteriorating due to repeated passages across the phase boundary.) KNO_3 -III, metastable at room T and p, could be prepared by first exposing the crystals to high pressure (2 - 4 kbar) at 130°C . Typical spontaneous polarization values for the metastable form ($\sim 4.5 \mu\text{Coul/cm}^2$) compare favorably with polycrystalline KNO_3 on a metal substrate ($3.5\text{-}6 \mu\text{Coul/cm}^2$). Phase III persisted for 10 - 20 minutes after exposure to the lower pressure and considerably longer after a pressure of 4 kbar.

Transitions across the II - III - IV and IV - III boundaries were so sluggish that little information could be gained.

In NaNO_2 , the III - II - I phase boundaries were well studied, so this work focused on the other ferroelectric boundary (III - IV). At atmospheric pressure, the transition is difficult to detect via dielectric anomalies. The same is true at higher pressures. At 13 kbar, no distinctive feature for ϵ was observed at the transition, but the top of a broad loss tangent peak did coincide with the boundary.

Large anomalies in both ϵ and $\tan \delta$ were observed at 3.5 to 4 kbar and 25°C (well away from a phase boundary). The location of these anomalies was temperature dependent. The cause of these anomalies was traced to the presence of water in the hygroscopic NaNO_2 . By drying both the specimen and the pressure fluid, the anomalies could be made to disappear.

The question of ferroelectricity in phase IV could not be answered by these measurements since $E_c(p)$ rises fairly rapidly. A value of $dT_0/dp = 4.2^\circ\text{C}/\text{kbar}$ was calculated from the pressure dependence of $P_s(T)$. This value is somewhat lower than those determined from dielectric and x-ray measurements.

This portion of the project formed the thesis research of James T. Leong. It has been accepted for publication as "Temperature and Pressure Dependence of the Dielectric Constant and Spontaneous Polarization of Ferroelectric KNO_3 and NaNO_2 ", James T. Leong and R. M. Emrick, J. Phys. Chem. Solids, in press.

(Copies of corrected copies of galley proofs of this article are included with this report. Reprints will be furnished as soon as they are available.)

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STUDENTS WHOSE Ph.D. THESES RESEARCH WAS SUPPORTED BY THIS CONTRACT

Brent J. Buescher - 1969

Patrick B. McArdle - 1969

James T. Leong - 1970

Carl N. Helmick, Jr. ---