AD-A035 078 OFFICE OF NAVAL RESEARCH LONDON (ENGLAND) F/G 11/6
SACLAY CONFERENCE ON DIFFUSION IN CONDENSED MEDIA.(U)
DEC 76 L SLIFKIN
UNCLASSIFIED ONRL-C-33-76 NL

1 OF 1
AD-A
035 078

END
DATE
FILMED
3-8-77
NTIS

SACLAY CONFERENCE ON DIFFUSION IN CONDENSED MEDIA

OFFICE OF NAVAL RESEARCH
LONDON, ENGLAND

17 DECEMBER 1976

ONR LONDON CONFERENCE REPORT

C-33-76

OFFICE OF NAVAL RESEARCH

BRANCH OFFICE LONDON ENGLAND

SACLAY CONFERENCE ON DIFFUSION IN CONDENSED MEDIA

PROFESSOR LAWRENCE SLIFKIN*

17 DECEMBER 1976

*University of North Carolina
Chapel Hill, North Carolina

UNITED STATES OF AMERICA

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE *(When Data Entered)*

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER ONRL-C-33-76	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE *(and Subtitle)* SACLAY CONFERENCE ON DIFFUSION IN CONDENSED MEDIA		5. TYPE OF REPORT & PERIOD COVERED
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) PROFESSOR LAWRENCE SLIFKIN		8. CONTRACT OR GRANT NUMBER(s)
9. PERFORMING ORGANIZATION NAME AND ADDRESS Office of Naval Research, branch office London Box 39, FPO New York 09510		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
11. CONTROLLING OFFICE NAME AND ADDRESS		12. REPORT DATE
		13. NUMBER OF PAGES 15
14. MONITORING AGENCY NAME & ADDRESS *(if different from Controlling Office)*		15. SECURITY CLASS. *(of this report)*
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT *(of this Report)*

APPROVED FOR PUBLIC RELEASE; DISTRIBUTION UNLIMITED

17. DISTRIBUTION STATEMENT *(of the abstract entered in Block 20, if different from Report)*

18. SUPPLEMENTARY NOTES

Topics studied include the following:

19. KEY WORDS *(Continue on reverse side if necessary and identify by block number)*

Diffusion in solids
Self-diffusion
Hetero-diffusion
Irradiation effects on diffusion
Diffusion theory
Techniques for measurement of diffusion
Superionic conductors
Amorphous materials
Surface diffusion
Grain boundary diffusion

20. ABSTRACT *(Continue on reverse side if necessary and identify by block number)*

This report on the 19th Colloque de Métalluigie, held by the Institut Naturial des Sciénces et Techniques Nucleaires in June 1976, briefly summarizes the review lectures and focuses attention on the main results reported in the poster sessions. A picture is thus given of the rather extensive interests and developments in France in the general area of diffusion in solids.

Continued

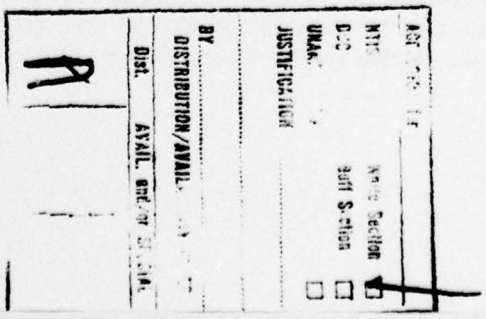
DD FORM 1 JAN 73 1473 EDITION OF 1 NOV 65 IS OBSOLETE S/N 0102-014-6601

SECURITY CLASSIFICATION OF THIS PAGE *(When Data Entered)*

The French counterpart to the American research facilities at Oak Ridge, Argonne, or Brookhaven is a large complex, the Centre d'Etudes Nucléaires de Saclay, located 2 km from the tiny village of Saclay, on a fertile plain about 20 km southwest of Paris. (Saclay also happens to be just north of the route taken by Gen. LeClerc's division in their drive to liberate Paris; in fact, the laboratory is within view of a memorial to a Free French soldier who was struck down at that point.) Associated with the CEN is the Institut National des Sciénces et Techniques Nucléaires, which, during 22-25 June 1976, sponsored its 19th Colloque de Métallurgie. This year's topic, organized by J.L. Bocquet and Y. Adda (CEN-Saclay), was "Diffusion in Condensed Media." The format consisted of a number of invited review papers, about half given by visitors from abroad, accompanied by poster sessions of related contributions which presented new research results from laboratories all over France. Since most of the review lectures were primarily tutorial, no attempt will be made here to recount all of them in detail. Instead, the main results reported in the poster sessions will be outlined, thereby providing a picture of current interests and developments in France in the general area of diffusion in solids.

The poster session itself is still a novel vehicle for scientific communication, and there has been some debate about its advantages and disadvantages. The present author found it less of a mental strain than the usual sessions of oral presentations; on the other hand, one also feels some sympathy for those contributors who were unable to spend much time looking at the other contributions while theirs were on display, and who had to explain their results over and over again to successive inquirers. And in particular, I missed the occasional spirited, multi--antagonist debate that sometimes arises during a conventional oral session-in the case of the poster session, you can indeed argue with the author, but the 3-body and higher-order interactions are strongly attenuated.

In the opening review lecture, A.D. LeClaire (AERE - Harwell) discussed two types of anomaly in atomic migration in metals: (a) the non-linear Arrhenius plots (log D versus 1/T, where D is the diffusivity) that have been well established for self-diffusion in some metals, and (b) several different anomalies connected with the migration of solutes. There are two general categories of curved Arrhenius plots: (a) those cases such as Ag and Na, in which the curvature is relatively small and which may be interpreted either in terms of a temperature-dependent activation energy or a divacancy contribution, and the (b) very large curvatures observed for a number of bcc transition metals. In this latter case, there may again be a second mechanism involved (divacancies, dislocations, interstitials, or extrinsic vacancies), or one may be witnessing a major decrease in the vacancy formation energy as the phase transition temperature is



approached from above. LeClaire argued that this second possibility was more compatible with the experimental facts. As for strange effects with solutes in non-abnormal solvents, he noted that in Al the effective charge of solutes is approximately independent of valence; this effect can be understood in terms of the electrostatic screening. The other solute anomaly discussed was that of the extremely rapid diffusion of noble metals in such polyvalent metals as lead and time, which appears to be due to a complex defect of the interstitial type.

During the related poster session, D. Ablitzer, J. Haeussler, and A. Vignes (Ecole Nat. Sup. de la Métall. et de l'Industrie des Mines - Nancy) presented results on the non-linear Arrhenius diffusion of V and Fe in V and in V/Fe alloys. In this case, even though vanadium does not show a change of phase, the Arrhenius plot is quite anomalous. Moreover, their data were better fit by two straight lines than by a continuously curved one, and could be interpreted satisfactorily in terms of the simple vacancy model earlier proposed by LeClair and Jones. A second paper by Ablitzer dealt with diffusion in Nb, which also does not exhibit a phase change. In this case, the Arrhenius plot is linear, but the diffusivity of Fe in Nb is anomalously large. From measurements of the diffusivities of both Fe and Nb, the effect of additions of Fe on the self-diffusion of Nb, and the isotope effect, Ablitzer concludes that the Fe migrates by means of a dissociative mechanism in which there is a small concentration of interstitials, which in this particular case appear to be bound to a nearby vacancy. Abilitzer and M. Gantois compared self-and hetero-diffusion on Nb and Ta by two different techniques radiotracers and the microprobe. It is reassuring that both methods gave the same results and also confirmed earlier work of Lundy *et al*,and Peart *et al*. The solidus rule of Roux and Vignes also fit their data very well. Self-diffusion in several rare earths (Ce, La, Yt, Gd) and actinides (Pu, Np) was measured by G. Marbach, M. Boidron, M. Fromont, and D. Calais (CEN - Fontenay-aux-Roses). They find that, whereas the D's are normal in the low-temperature compact phases, the high-temperature bcc phases show unusually large D's (exceeding 10^{-7} cm^2/sec before melting) and small activation energies Q (about one-half the usual $34T_m$). It had earlier been proposed that the high D's in the actinides are due to easy promotion of f-electrons, but since the same phenomena are found here in the electronically stable La and Gd, the authors prefer an explanation based on a more complex defect, such as highly relaxed vacancy or a defect cluster. In an accompanying paper, this group plus J. Zanghi show that the correlation: $\Delta V(\text{diffusion})/\Delta V(\text{fusion}) = Q(\text{diffusion})/\text{latent heat of fusion}$, is in excellent agreement with experimental data on the rare earths and actinides, for fcc and bcc structures, for the pure metals and dilute alloys, and encompassing a range of volumes of fusion from negative to positive. Both self-diffusion and the heterodiffusion of Co, Ag, and Au in Pu and Ce were reported by G. Marbach, C. Charissoux (CEN- Fontenay-aux-Roses), and

C. Janot (University of Nancy). In several of these cases the solute diffuses much more rapidly - sometimes by several powers of ten - than does the solvent, suggesting the operation of some sort of interstitial mechanism. An analysis of non-linear Arrhenius behavior in bcc Mo, Nb, Ta, and W, in terms of Kidson's model of impurity-introduced vacancies, was given by B. Lesage and A. Huntz (Orsay).

A study of the effects of pressure, alloying, and irradiation on the anomalously rapid diffusion of gold in lead was described by A. Barbu (CEN-Saclay). He confirmed Warburton's observation that D decreases linearly with increasing concentration of Au; at 150°C, the parameter "b" has the value -2000. In pure Pb, Barbu finds that the volume of activation at 200° C, measured up to 8 kbar, is only 0.28 times the atomic volume. He also finds that, whereas the non-irradiated specimens show non-gaussian penetration profiles, those that have been neutron-irradiated have a much higher solubility for Au and also give gaussian penetrations -- all of this suggests that the irradiation dissociates the complex defects known as diplons. A more refined calculation of the correlation factor for anisotropic diffusion, in terms of the various jump frequencies, was given by J. Bocquet, P. Benoist, and P. Lafore (CEN - Saclay). The resulting more-nearly-exact expressions are particularly important for the case of migration along a boundary. A. da Fano and G. Jacucci (Orsay) presented the results of a computer simulation of vacancy dynamics in a fcc metal at high temperatures, in which the vacancy was in each case followed for about 300 jumps. They see a number of rather complicated features, such as: (a) passage over the col and then an immediate return on the same jump; (b) a dynamically correlated double jump of the vacancy, in which there is a noticeable persistence in the momentum; i.e., jumps involving the displacement of more than one atom. These multiple jumps have a higher effective activation energy than do the simple jumps, and just below the melting point they are seen to contribute about 10% of the total diffusion. The authors point out that these effects could be involved in non-linear Arrhenius plots and in a temperature-dependence of the correlation factor.

Evidence for deviations from local equilibrium at diffusion interfaces in multicomponent systems, along with a thermodynamic analysis, was reported by D. Marchive, D. Treheux, D. Duc-Juve, and P. Guiraldenq (Ecole Centrale de Lyon). In a second paper from this laboratory, J. Godet, Treheux, and Guiraldenq studied the internal oxidation of various chrome-nickel steels, monitoring the process by the precipitation of oxides of Al or Si, and analyzing the results by means of the theory of C. Wagner to obtain the diffusivity of oxide ion as a function of composition and partial pressure of oxygen.

A. Seeger (Stuttgart) reviewed how one can get information about vacancies from their capture of positivity charged subatomic particles.

In the now well-known case of positrons, one can measure the lifetime, the Doppler broadening of the subsequent gamma rays, and the angular correlation. Protons and deuterons can be studied by NMR or mechanical or magnetic relaxation methods. The positive muon, which can be regarded as a sort of light isotope of hydrogen, is also captured by the vacancies, and its polarization in an external magnetic field can be observed by monitoring the anisotropy of the emitted positrons; this experiment is equivalent to a very sensitive NMR, yielding T_1 and T_2, which give information about the migration and trapping of the muon. One possible interpretative difficulty, which was pointed out from the floor by M. Stoneham, is that the very large zero-point energy of the muon may cause it to choose a stable site that is different from that of ordinary hydrogen, thus rendering dubious any comparison of the dynamics of the two different "isotopes."

Recent advances in techni-ues for determining diffusivities, especially in cases where the D's are very low, were reviewed by J. Philibert (CNRS - Bellevue). The new techniques include (a) electrochemical sectioning (30-A slices), for measurement of D's down to 10^{-18} cm^2/sec; (b) sectioning by ion sputtering; (c) analysis near the surface, using such methods as SIMS (secondary ions by mass spectroscopy), AES (Auger slectron spectroscopy), or elastic backscattering; (d) neclear reactions, when there is a resonance cross section; (e) Mössbauer effect; and (f) shrinkage of dislocation loops. Philibert also discussed the older methods of NMR and mechanical or electrical relaxation, which all are sensitive to single jumps per atom.

In the accompanying poster session, Y. Limoge, R. Seguin, and J. Seran (CEN - Saclay) gave evidence of an irradiation-induced diffusion which is produced during use of an ionic analyzer; such effects must be recognized if several of the techniques discussed above by Philibert are to be used to measure very small diffusivities. In the present experiments, displacements produced by the primary beam were observed for Si^*O_2 on both SiO_2 and Si and also for Cu on Al. In the first case, radioactive Si could be detected at depths considerably greater than the range of the primary beam there are also effects due to enhanced defect concentrations resulting in an irradiation-enhanced diffusivity. In the review lecture of Philibert, there had also been some discussion of the observation that techniques such as NMR and Mössbauer spectroscopy often give diffusivities that do not agree with those obtained by radiotracer methods. Further insight into this problem was provided by a computer simulation, using a model potential appropriate to aluminum, and performed by A. da Fano and G. Jacucci (CECAM - Orsay). This work showed that NMR and Mössbauer results are significantly affected by non-diffusive lattice vibration, motions that do not contribute to the radiotracer diffusivity. Finally, C. Roques-Carmes, J. Pivin, and P. LaCombe (Orsay) showed how two different techniques of micro-analysis, secondary ion emission and electron microprobe, could yield complementary information

on the composition and structure of oxide layers formed on such alloys as Ni-Cr and Fe-Ni-Cr.

Mass transport in essentially two-dimensional structures (e.g., free surfaces, grain boundaries, phase boundaries, and thin films) was reviewed by G. Martin and B. Perraillon (CEN - Saclay). They pointed out the difficulties of characterizing the structure and chemical composition of such systems, of obtaining diffusivities by a direct method, and of developing appropriate models for the analysis of experimental results. Recent work on the transport-related properties of free surfaces includes field-ion microscopic observations of adatoms and pairs, with an anisotropy of jump frequency, and the demonstration of a spectacular effect of adsorbed impurities on surface diffusion. One important unanswered question about surface diffusion is whether the observed diffusivity is limited by the migration between steps on the surface or by the adsorption-desorption equilibrium at the steps. With regard to grain boundaries, Martin discussed the complicated structure, the problem of solute segregation, and recent developments on the descriptions of boundaries in terms of dislocation networks and coincidences. Turning to thin films, the question of longitudinal versus transverse diffusivities was touched on.

The poster session did not include any contributions on diffusion in thin films, but did contain several papers on surfaces and grain boundaries. J. Cousty, R. Peix, and B. Perraillon (CEN - Saclay) described an experiment on vicinal copper surfaces of very carefully controlled purity and orientation, monitored by LEED and Auger electron spectroscopy. The concentration of surface solute was maintained at less than 0.001 monolayer. Preliminary experiments on diffusion of radiotracers on such surfaces yielded D's which agree with the earlier values of Goesting, who had only less clean surfaces at his disposal. J. Jaunet and C. Waldburger (CNRS - Bellevue) used the scratch-smoothing kinetics to determine surface diffusion on 5-nines nickel under a vacuum of 10^{-8} torr. The grooves were produced by photogravure plus electrolytic polishing, and all measurements were confined to those regions over which the groove amplitude was constant. Further, the groove spacing was chosen such that at the experimental temperature, surface diffusion would dominate over evaporation and volume kinetics in the decay kinetics of the grooves. They found that the surface diffusivity decreases with time during the early stages of the run, apparently an effect of the segregation of impurities to the surfaces. For the steady state, they find that $D_s = 7.5 \exp(-35.3 \text{ kcal/RT}) \text{ cm}^2/\text{sec}$. Thus, the observed activation energy is about half that for bulk diffusion. The groove produced where a grain boundary intersects the crystal surface was studied by V. Binh (Univ. of Lyon), both with regard to its profile and also the kinetics of its formation. Binh finds deviations from the prediction of the theories of Mullins and Robertson and is now performing experiments on the roles of macroscopic surface morphology (using cylindrical specimens) and of evaporation.

The effect of a solute on grain boundary diffusion -in this case, the effect of Sn on grain boundary self-diffusion in Ag -- was discussed by P. Gas and J. Bernardini (Univ. of Marseille). The necessity of complete elucidation of the segregation of the solute to the boundary was emphsized. Their results indicate that the grain boundary diffusivity increases approximately linearly with tin content, but that for solute concentrations exceeding 10^{-3} the boundary is completely saturated with tin. In another paper from Marseille, by A. Rolland, Bernardini, and F. Cabané-Brouty, solute segregation at the free surface was considered. Some solutes, such as sulfer and oxygen, show a strong affinity for metallic solvents and can form surface compounds even under conditions in which the corresponding 3-dimensional compound is unstable. An example of the opposite extreme, where there is only a weak affinity between solute and solvent, is Ni in Ag, the system studied here. The authors found that for nickel-doped silver specimens annealed in hydrogen, the surface concentration of the solute was about 10^4 times that in the bulk. The effects of segregation and precipitation of carbon in iron alloys and Ni-Cr alloys were explored by a large group working with Prof. P. LaCombe (Orsay). They have obtained results on the effects of carbide precipitation on boundary and surface diffusion, on phase transitions, and on the trapping of hydrogen. A calculation of the anisotropic grain boundary diffusivity as a function of the various possible jump frequencies was reported by V. Coste, P. Benoist, and G. Martin (CEN - Saclay). The calculation was performed for the (012) twin boundary of a hypothetical simple cubic lattice. The ratio of the diffusivities parallel and perpendicular to the axis of twist depends on the ratios of the jump frequencies within the boundary but is independent of the geometry of exchanges between the boundary and matrix, although the individual D's do depend strongly on this geometry.

As an example of an industrial application, A. Accary (Univ. of Clermont-Ferrand) discussed the role of diffusion in the sintering of metal powders. One large problem is how to set up a model which takes into account the variety of shapes and metallurgical characteristics of the particles. Moreover, it is difficult to predict mechanical properties and swelling. Finally, not only can diffusion theory be used to elucidate sintering partially, but also there are sintering phenomena which raise new questions about diffusion processes.

A session on the effects of irradiation on diffusion was initiated with a review paper by G. Brébec and Y. Adda (CEN - Saclay) in which they treated not only the usual effects of enhanced point defect concentrations but also the increase in defect mobility during irradiation. This comes about because a sub-threshold collision can induce a vacancy jump; in addition, in semiconductors, there are also electronic effects influencing defect migration. Following this lecture, a beautiful computer-produced film illustrating several of these effects was shown by N. Doan (CEN - Saclay). In the poster session, P. Baruch (ENS - Paris) gave a simple theory of the effect of the inhomogeneity of

point defect concentration which is produced during irradiation by a beam of charged particles. The resulting flux of point defects produces an anisotropy in migration of solute atoms and a Kirkendall-like effect. Recent experimental results on bombarded doped silicon can be interpreted either in terms of the gradient in concentration of a single type of defect or, alternatively, in terms of a competition between two different mechanisms of diffusion.

Anelastic relaxation in a binary alloy (the Zener relaxation) provides a very sensitive monitor of point defect concentration, since the relaxation time is only of the order of the mean jump time for an atom. M. Halbwachs, J. Hillairet, and J. Cost (CEN - Grenoble) used this technique to study the effect of electron irradiation on the concentration of point defects in Ag-Zn, with an apparatus that could detect changes of defect concentrations as small as one point defect per 10^{10} atom sites. Their experimental scheme involved following the length relaxation of a stressed specimen as point defect migration produced local redistributions in the alloy. By observing the build-up and decay of point defects when the irradiating beam was turned on and off, all as a function of temperature, they could demonstrate the effects of both vacancies and interstitials, measure their lifetimes and mobilities,and evaluate the mechanisms of their elimination (recombination and trapping at sinks). D. Esteve and F. Saint-Yves (Lab. de Phys. des Solides - Toulous) measured the effect of low energy protons (less than 100 keV) on the diffusion of boron in silicon at high temperatures, analyzing the results in terms of both interstitial and substitutional boron, and making use of a computer simulation to compare experiment with predictions from their model. Another computer simulation of irradiation effects, this time done for a model for copper, was described by A. Tenenbaum (CECAM - Orsay) and N. Doan (CEN - Saclay). They find focused collision sequences occur up to a temperture of about one-third of the melting point. They also observe induced vacancy jumps resulting from sub-threshold collisions; for electron irradiation, this effect is very sensitive to orientation and to the energy of the incident beam (the probability goes through a maximum for incident electrons of about 60-100 keV).

With especial reference to the processes of diffusion of gas atoms in solids, A.M. Stoneham (Harwell) reviewed recent theoretical developments: better methods for the calculation of defect parameters, more refined analysis of solid state processes, and a treatment of quantum effects. He discussed in some detail two types of system: rare gases in ionic crystals and the diffusion of H and H_e in metals -- it is for such light atoms that the quantum effects become important. The more traditional approaches, phenomenological (Fick's laws, irreversible thermodynamics) and empirical theories (Arrhenius plots, law of mass action), have now been supplemented by improved microscopic theories which often include calculation of electronic effects, many-body interactions,

and details of atomic motions. There are still, however, complications in dealing with quantum mechanical effects, with the effects of charge state on activation energy in semiconductors, with complex defects such as are found in $Fe_{1-x}O$, with trapping effects, and in more complex situations in which the observed activation energy is not the height of the col.

After this lecture, there was then a poster session which consisted of two papers on hydrogen in metals. M. Jerome, J. Galland, P. Azou, and P. Bastien (Ecole Centrale - Chatenay-Malabry) followed the permeation of hydrogen through Armco iron by an electrochemical technique. The resulting D's were lower than generally accepted, and presumably reflected a trapping effect. Their results also showed a non-instantaneous build-up of hydrogen concentration at the surface of entry. The other paper, by E. Liegon (CEN - Grenoble), dealt with hydrogen implanted in aluminum, using both ordinary hydrogen and deuterium, and analyzing the implantation profile by means of nuclear reactions (depth resolution = 500 A). They found that for implantation temperatures less than 180 K, the hydrogen occupies a tetrahedral site, possibly involving vacancies created by the implantation. At higher temperatures, the hydrogen migrates over long sistances and becomes trapped at the surface.

Three papers considered the study of atomic diffusion by computer simulation experiments. Two of these, by C. Bennett (IBM) and by A. Rahman (Argonne), were invited reviews, while the third, by A. da Fano and G. Jacucci (CECAM - Orsay), was presented in an earlier poster session. In such computer experiments, one can set up a model interionic interaction which takes into account the anharmonicities, which can be important at high temperatures; in fact, Bennett argued that the omission of anharmonic effects results in a greatly underestimated value for the concentration of vacancies at high temperatures and a greatly overestimated value for ΔK (the factor which arises from an isotope experiment, and which is approximately associated with the fraction of the activation energy of migration which is actually carried by the jumping atom). The role of multiple jumps, whereby the vacancy makes two or more dynamically correlated jumps in sequence, has already been discussed above in the report of the da Fano-Jacucci paper. These jumps become more important at high temperature, thereby leading to a temperature dependence of both ΔK and the activation energy; it was suggested that they are involved in the peculiar behavior of self-diffusion in sodium (large increase in activation energy with temperature, and small value of ΔK). Bennett also argued from his computer studies that there is no substantial contribution from divacancies to the self-diffusion of sodium, contrary to some recent interpretation.

Four papers dealt specifically with semiconductors. J. Corbett (SUNY - Albany) and J. Bourgoin (ENS - Paris) reviewed the situation with regard to Ge and Si, noting that even at this late date there

is still disagreement -etween theory and experiment on the activation energy and pre-exponential factor for self-diffusion in Si. For solutes diffusing in these crystals, charge effects are much more important than mass or radius, and are probably the basis for the large diffusivities of interstitial transition metals in Ge and Si. The technological aspect of diffusion in semiconductors was considered by J. Gailliard (CEN - Grenoble). As examples of problems encountered in device fabrication, he cited difficulties in the control of impurity distributions and the perturbations of solute penetration both by crystal defects and by variations in properties at the crystal surface and in the initial deposited layer of dopant. One of the poster papers, by L. Svob and C. Grattepain (Bellevue), presented experiments on the diffusion of Li into non-stoichiometric CdTe at 300°C. The diffusion profiles can be decomposed into two components: one due to a species present at high concentration but having a small diffusivity, and another at low concentration but possessing a high D. The results of variations of the stoichiometry of the CdTe, plus the comparison of the results with a model due to Kucher, have led the investigators to suggest that the first species is some sort of vacancy-type defect, while the second is an interstitial. The second poster paper reported results on the interstitial diffusion of Au in Si, by J. O'Brien and J. Bourgoin (ENS - Paris). Their measurements were conducted at relatively low temperatures, using the capacitance versus voltage of Schottky diodes to monitor the diffusion.

Diffusion in simple halides and oxides was reviewed by L. Slifkin (CEN - Saclay & Univ. of NC), with emphasis on the contrast between phenomena in such crystals, where the defects are electrically charged, and the corresponding case of metals. He discussed current controversies over defect actimation energies and their temperature-dependence, the role of electrical charges on surfaces and dislocations, the kinetics of defect aggregation, and the role of the crystalline electric field. There were four accompanying poster papers on ionic crystals. A. Laskar, D.Foster, and K. Wagner (Clemson) described the ionic conductivity and cation tracer diffusion in potassium and rubidium azides, in which Schottky defects are present and the cation vacancy produces the conductivity. For KN_3, the Schottky defect formation energy is 1.6 eV; the cation vacancy migration energy is 0.6 eV parallel to the c-axis and 0.7 eV perpendicular to it. The corresponding values for the rubidium salt are each 0.1 to 0.2 eV higher. The self-diffusion of oxide in NiO was reported by C. duBois, S. Barbezat, R. Talon, and C. Monty (CNRS - Bellevue). Previous work on this problem had been by means of oxygen isotope exchange, but such an experiment is blind to any penetration anomalies that might be present. In the present work, the actual penetration profile was obtained by use of an ion analyzer to measure the concentration of ^{18}O. The resulting D's are some 100 times smaller than the earlier values obtained by isotope exchange. The effects of implantation of alkali ions in AgCl were studied by J. Gisclon and J. duPuy (Univ. of Lyon), using optical absorption, EPR, frequency-dependent ionic

conductivity, and dc polarization. The conductivity was measured over the very wide range of 0.01 to 10^7 Hz, and the results were analyzed in terms of silver aggregates produced by the ion beam. In another paper from Lyon, the effects of implantation of potassium in MgO were explored by P. Thévenard, J. duPin, A. Cachard, and J. Davenas. Optical absorption shows that as one anneals such implanted crystals above 500°C, small clusters of potassium atoms begin to form; when these clusters grow to about 500 atoms, they behave like metallic particles.

Four papers were concerned with "superionic" conductors. The general subject was reviewed by D. Lazarus (Univ. Illinois), who emphasized those substances showing a phase transition from a normal to a highly conducting phase. He pointed out that for many of these materials, it is the anion that is the highly mobile species, migrating interstitially in an ordered cation lattice. Two poster papers specifically dealt with beta-aluminas, in which the conductivity is by means of a mobile monovalent cation moving through specific conducting planes. A large group working with A. Guinier (Orsay) described x-ray scattering experiments which showed that at 20 K, the mobile cation is partially ordered in the conducting plane; this order decreases as the temperature is raised and the conductivity increases. Another group from Orsay -- L. Zuppiroli, G. Deplanque, D. Jerome, and J. Boilot -- also studied the distribution of sodium ion in beta alumina, in this case by means of NMR. Their results give strong evidence of a clustering into triatomic equilateral triangles, this triangular clustering presumably being of importance to the diffusion and ionic conductivity process. The fourth paper was on the mobility of fluoride ion in $Na_{1-x}Y_xF_{1+2x}$ (i.e., $NaYF_4$ doped with YF_3) and was presented by Y. Chabre and C. Berthier (Univ. of Grenoble). These authors used NMR techniques to measure T_1 and T_2 as a function of temperature, and get values of the migration activation energy in the range 0.4 to 0.5 eV, about 2/3 that deduced from the ionic conductivity. In impure crystals, however, the NMR value is substantially that obtained from conductivity analysis; in this case, both phenomena are dominated by migration of impurities. At high temperatures, above 700°C, the conductivity activation energy drops to about 1/4 eV, but the NMR results do not show a corresponding change.

The effect of electric fields and thermal gradients on the drift of atoms in crystals has long been a topic of research at Saclay. These phenomena are not simply esoteric curiosities, but cause great difficulties in the thin film connectors of integrated circuits and in the fuel elements of nuclear reactors, in which both T and grad T can be quite large. Both the scientific and the technological aspects of atom drift under the influence of applied fields were discussed by N. Doan, J. Bocquet, and Y. Limoge (CEN - Saclay). Limoge also offered a poster paper on electromigration of various tracers in aluminum. The results were analyzed to give effective valences; these values could only be understood if one takes into account the effect of the

non-sphericity of the Fermi surface on the effective valence. In another poster paper, E. Mathe (Univ. of Poitiers) analyzed the effect of a temperature gradient on precipitation of a solute from a supersaturated solution. He showed how the resulting precipitate would be non-uniformly distributed, depending on the geometry of the experiment, and how the kinetics of the growth of the particles would be perturbed. M. Balourdet, Y. Malmejac, and P. Desre (CEN - Grenoble) described experiments on the thermodiffusion of tracers of Ag, In, and Sb in liquid tin, using the capillary method. For Ag in liquid Sn, the direction of migration reverses as the temperature is increased above 600°C. This comes about because of the competition between two terms: one involves the interaction of the migrating ion with the other ions, and gives a heat of transport varying linearly with T; the second is an electronic effect, and varies as T^2. This electronic term can be understood in terms of Gerl's theory and Ziman's nearly-free-electron model. Experiments were also carried out in a liquid Ag-Ge alloy, but here the electronic structure is more complicated, and the term in T^2 was not well predicted by the Ziman theory.

Diffusion in amorphous materials was surveyed by J. Cornet, J. Escanye, and M. Gerl (Univ. of Nancy). In contrast to metallic liquids, where the diffusivities are large, where also several experimental techniques are available, and where a number of theoretical models have been proposed, the situation for solid amorphous substances is much less favorable. For the amorphous solids there is no good theory, the unpleasant mechanical properties make measurement difficult, and the diffusivities are not very large (they are more like those of crystalline solids than metals). One thus uses rather non-conventional methods, such as ion backscattering, electronic emission, or secondary ion emission. The results are often interpreted in terms of percolation theory, but one must also consider the effects of chemical reaction, crystallization, surface phenomena, and differences in electronegativity. The Nancy group also had a paper in the poster session in which they reported on the diffusion of various solutes in liquid tin, using a thin film of tracer and an elegant shear cell. They find that, in contrast to the case for solid hosts, the diffusivity is not very sensitive to the valence of the solute. The diffusion of lithium in amorphous $Pd_{80}Si_{20}$ was measured by C.Birac and D. Lesueur (CEN - Fontenay-aux-Roses). Over the temperature range 240 to 290°C, D was found to be about 100 times its value in the crystalline material and its temperature-dependence was found not to obey the Arrhenius law.

The final session of the Conference dealt with practical problems. M. Aucouturier (Orsay) and P. Guiraldenq (Ecole Centrale - Lyon) discussed the role of diffusion in the metal-to-metal contact and in various technilogical surface treatments. They considered formation of chemically different layers on the surface, effects on adherence and mechanical properties, corrosion resistance, friction, diffusion during rubbing, diffusion welding, and tool wear. Guiraldenq's group also contributed

a poster paper on the diffusion of Sn, Ag, and F^- from a dental amalgam into the tooth's enamel and dentine. They find that Ag is quite immobile, Sn has a substantial mobility, and fluoride is extremely mobile, becoming homogeneously distributed in about two months. The Lyon group also presented a paper on diffusion phenomena during frictional welding, pointing out the complications due to large gradients of temperture and pressure. They have performed experiments on the diffusion of radio-carbon during friction welding followed by forging, and find that the diffusion range of carbon is very large, several hundred microns. A final paper, by D. Boutard, J. Galland, P. Azou, and P. Bastien (Ecole Centrale Chatenay-Malabry), dealt with the effect of friction on the corrosion of a stainless steel in 1 N H_2SO_4. In the absence of friction, the steel quickly becomes passive in this medium, but frictional rubbing greatly enhances corrosion, the speed of the corrosion reaction depending on the speed and pressure of the rubbing. One thus must consider carefully the kinetics of the surface reactions in order to explain the effects of friction on corrosion.

Looking back on the Conference, which was efficiently and amiably organized, one is tempted to speculate as to whether we did not generate a great quantity of hot air - because the ending of the meeting coincided with the beginning of the hottest spell of weather that Paris has seen in decades!