PHYSICAL REVIEW B VOLUME 36, NUMBER 7 1 SEPTEMBER 1987

Brief Reports

Brief Reports are short papers which report on completed research which, while meeting the usual **Physical Review** *standards of scientific quality, does not warrant a regular article. (Addenda to papers previously published in the* **Physical Review** *by the same authors are included in Brief Reports.) A Brief Report may be no longer than 3½ printed pages and must be accompanied by an abstract. The same publication schedule as for regular articles is followed, and page proofs are sent to authors.*

Separate migration and formation energies of vacancies in aluminum measured by NMR

Terry W. Gullion
Department of Chemistry, Washington University, St. Louis, Missouri 63130

Mark S. Conradi
Department of Physics, Washington University, St. Louis, Missouri 63130

(Received 5 February 1987)

After a rapid change in temperature of a crystalline solid, the rate of vacancy motion changes immediately while the concentration of vacancies changes more slowly. We report NMR diffusion measurements on pure aluminum foil done at constant vacancy concentration by rapid rf heating from a constant preparation temperature. Thus, the temperature dependence of the diffusion yields the migration energy E_M. Our results for E_M, 0.71 and 0.66 eV, are in good agreement with the accepted value. The experiment reported here should be applicable to all kinds of solids, provided a means of rapid heating or cooling is available.

Diffusion in most crystalline solids proceeds by a defect, either a vacancy or an interstitial.[1] For diffusion to occur a defect must be formed, with activation energy E_F, and the defect must migrate amongst the equivalent sites, requiring activation energy E_M. Thus, the activation energy E_D describing the temperature variation of diffusion is the sum of E_F and E_M. We present here a technique for separately determining E_F and E_M which should be applicable to essentially all solids.

We consider the case of monovacancy diffusion, the diffusion mechanism of most pure materials.[1] At any nonzero temperature, vacancies exist at thermodynamic equilibrium with concentration X given by[2]

$$X = e^{-E_F/kT} . \tag{1}$$

The activation energy E_F is closely related to the binding energy of the solid. Any vacancy in the solid executes site-to-site jumps at rate ω_v,

$$\omega_v = \omega_0 e^{-E_M/kT} . \tag{2}$$

The attempt frequency ω_0 is often approximated by the Debye cutoff frequency; the migration energy E_M is often not very different from E_F. The rate at which any typical atom in the solid jumps is just

$$\omega_j = X\omega_v = \omega_0 e^{-(E_F+E_M)/kT} . \tag{3}$$

In a more complete analysis,[2] entropies of activation and/or temperature-dependent activation energies arise; the effect of these can be lumped into the prefactor ω_0 which may then differ by one or two orders of magnitude from vibrational frequencies. Measurements of the temperature dependence of diffusion yield $E_D = E_F + E_M$ and are fairly common.[3] Coupled with a determination of either E_F or E_M, the other energy (E_M or E_F) is then obtained.

There are several methods for measuring E_F or E_M. The concentration of vacancies may be directly determined by comparing the bulk thermal expansion coefficient and that of the x-ray lattice parameter.[4] This method has been used for metals[4-6] and for rare-gas solids.[7-10] In general, the method requires extremely high precision and is particularly difficult for materials that flow under gravity (e.g., molecular and rare-gas solids).

Ionic materials can have vacancies added chemically.[2] For example, the addition of KF to CaF_2 involves K^+ sitting on the Ca^{2+} sublattice with the production of a vacancy on the F^- sublattice. Over a range of temperatures, the F^- diffusion and ionic conductivity are dominated by the extrinsic vacancies and the temperature dependence of diffusion is determined by E_M alone. Of course, the Coulomb attraction of the vacancy to the K^+ complicates the issue, particularly at low temperatures. The chemical production of vacancies is only available with ionic solids.

In metals, vacancies created at high temperatures T_F may be frozen in by rapid quenching to a low temperature T_Q.[11] The concentration of vacancies can be determined from electrical resistivity measurements at low temperatures because vacancies scatter electrons.[12] Typically, the resistance of the quenched sample is compared to that of a reference sample at 77 K. The temperature (T_F) dependence of the vacancy concentration yields E_F.[13-15] By studying the time and temperature (T_Q) dependence of the low-temperature annealing out of the vacancies, E_M may be obtained.[16-18] Clearly, this technique is only available with metals. Finally, positron annihilation has been used to determine the vacancy concentration.[19-22]

None of the current techniques is satisfactory for all solids. For example, although E_F has been determined in rare-gas solids,[7-10] there are no measurements of E_F or E_M in molecular solids,[23] to our knowledge.

When the temperature of a solid is changed, the vacancies present change their jump rate ω_v almost immediately. Without direct evidence, it is reasonable that this change takes a few vibrational periods, about 10^{-12} s. By comparison, changing of the vacancy concentration is much slower. Naively, one would expect that vacancies diffuse to and from free surfaces or grain boundaries to come to equilibrium. Actually, dislocations are the most important sources or sinks of vacancies.[24] In well-annealed metal foils, quenching experiments found that the time constant for vacancy equilibration was of the order of 1 s.[24,25]

Our NMR measurement of E_M in aluminum involves preparing the sample at a variable temperature T_M with the (fixed) vacancy concentration appropriate to temperature T_F. The sample is initially at T_F and is then heated rapidly to T_M. At the temperature T_M the atomic jump rate ω_j is determined from a measurement of the dipolar order relaxation time T_{1D} of the nuclear spins. Because the heating from T_F to T_M is rapid, the vacancy concentration is expected to be unchanged. Thus, the jump rate ω_j at T_M is given by

$$\omega_j = X\omega_v = \omega_0 e^{-E_F/kT_F} e^{-E_m/kT_m} \; . \tag{4}$$

The temperature (T_M) dependence of the jump rate ω_j yields the migration energy E_M. During the course of this work, we learned of related but unpublished experiments on aluminum by Sun.[26]

The pulse sequence is shown in Fig. 1. The metal sample is rapidly heated from T_F to T_M with rf eddy currents from an 80-ms burst of rf magnetic field. By varying the duty cycle of the burst (chopped at 1 kHz) the final temperature T_M is controlled. As a matter of convenience the heating burst uses the same frequency (22 MHz), amplifiers, and rf coil as the NMR. The use of rf heating avoids the effects of forces and torques upon the sample that would occur with dc heating in the magnetic field. A relay bypasses the conventional crossed diode transmit-receive switches[27] during the long heating pulses. At the end of the heating burst, a 20-ms delay allows the bypass relay to deactivate, readying the NMR spectrometer. During the delay, the ^{27}Al spins return to equilibrium magnetization: The ^{27}Al T_1 is about 4 ms. To obtain sufficient heating we use a 1200-W amplifier, producing 80 G in the rotating frame. A particularly low L/C ratio is chosen for the tuned circuit to avoid rf breakdown.[27] The largest temperature jumps obtained after the delay are about 60 K.

After the 20-ms delay, the Jeener-Broekaert pulse sequence[28] is used to measure T_{1D}, the spin-lattice relaxation time of dipolar spin order. According to Slichter-Ailion slow-motion theory,[29-31] T_{1D} is determined by diffusion,

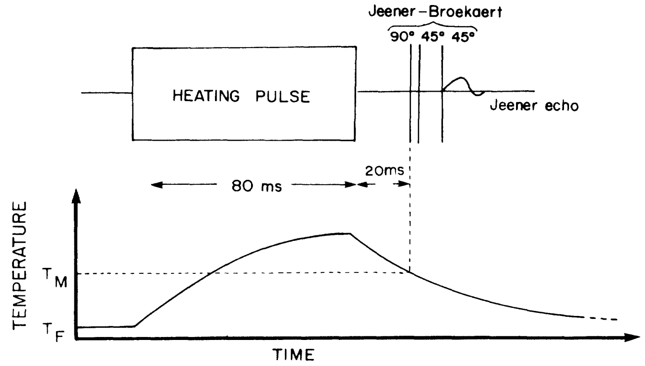

FIG. 1. Pulse sequence used in temperature-jump study of vacancy migration. A long rf heating pulse is followed by a delay; the Jeener-Broekaert sequence is then used to measure T_{1D} (essentially the atomic jump time τ_j). The lower part of the figure is a typical temperature-time plot for the aluminum foil sample. The time scales at top and bottom are the same. The Jeener-Broekaert sequence lasts typically 1 ms and has been exaggerated in the figure.

$$T_{1D}^{-1} = 2(1-p)\omega_j \; . \tag{5}$$

The factor p expresses the site-to-site correlation of local fields from the nuclear spins. There is an additional and undesired contribution from the conduction electrons:

$$T_{1D}^{-1} = 2T_1^{-1} \; . \tag{6}$$

The factor of 2 in Eq. (6) is justified for uncorrelated fluctuating hyperfine fields at neighboring spin sites.[32] The above processes are independent so their rates add. The observed relaxation rate T_{1D}^{-1} becomes

$$T_{1D}^{-1} = 2(1-p)\omega_j + 2T_1^{-1} \; . \tag{7}$$

Because we are only interested in the temperature dependence of ω_j to determine activation energies, we take $2(1-p)$ as unity. Defining $\tau_j \equiv \omega_j^{-1}$, Eq. (7) becomes

$$\tau_j^{-1} = T_{1D}^{-1} - 2T_1^{-1} \; . \tag{8}$$

Measurements of T_{1D} and T_1 allow determination of τ_j. We note that $\tau_j = T_{1D}$ in the limit of $T_{1D} \ll T_1$.

The sample was in the form of a pure aluminum foil 25-μm-thick (Alfa Chemicals, 99.999% pure). It was folded once about a thin mica insulator and placed in a glass test tube inside the rf coil. The rf magnetic field H_1 was nominally parallel to the surface of the foil everywhere, so the foil did not disturb the H_1 field lines. The H_1 homogeneity was determined to be $\pm 10\%$ across the length of the sample. The sample temperature was determined directly by measuring its resistance with a four-wire method in real time. A typical temperature-time plot is shown in Fig. 1. The sample resistance thermometer was calibrated against a thermocouple under equilibrium conditions. The background temperature T_F was established by blowing thermostated hot air past the glass test tube.

The temperature determined from the sample resistance is an average temperature across the sample. We presume the rf heating was uniform because of the uniform H_1 field and the alignment of H_1 parallel to the foil. Also, the thermal diffusivity $D_T \equiv \sigma/\rho c_p$ is about 1 cm^2/s for aluminum at 300 °C. Thus, in the 0.1 s of heating and delay a uniform temperature is established throughout the sample thickness. On the other hand, the $\sim$1.5-cm-long sample does not cool appreciably by conduction out its upper end. We note that the measurement times T_{1D} are very short compared to the cooling time constant in Fig. 1.

Before presenting the nonequilibrium results, we present in Fig. 2 equilibrium T_{1D} and T_1 measurements from the same foil sample used later in temperature-jump experiments. As expected from Eq. (8), at high temperature T_{1D} is determined by diffusion while at low temperature T_{1D} is very nearly $T_1/2$. The actual low-temperature T_1/T_{1D} ratio in Fig. 2 is 2.04, approximated throughout this work as 2 in agreement with Eq. (8). The T_1 data are in accurate agreement with previous results,[32,33] given by $T_1 T = 1.80$ sK; we show only the line representing this equation in Fig. 2. The diffusion jump time τ_j obtained from Eq. (8) is presented in Fig. 2. The activation energy of the Fig. 2 τ_j data, 1.33 ± 0.03 eV, is in excellent agreement with previous determinations.[3,33,34]

The nonequilibrium results are presented in Fig. 3. Two sets of data were obtained with preparation temperatures T_F of 526 and 542 K. The values of τ_j in Fig. 3 were determined from the T_{1D} of the nonequilibrium sample and the T_1 of equilibrium measurements. The lowest temperature (T_M) data point in each of the two data sets correspond to no rf heating and $T_M = T_F$. The slopes of the lines least-squares fit to the data represent activation energies of 0.71 and 0.66 eV.

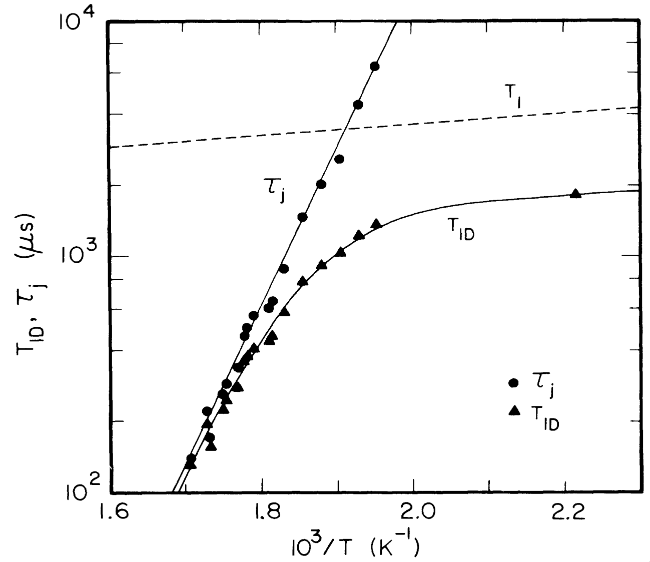

FIG. 2. Equilibrium T_1 and T_{1D} data for aluminum. The T_1 data are well represented by the dashed line, which corresponds to $T_1 T = 1.80$ s K. The T_{1D} data (▲) at low temperatures are limited by $T_1/2$, as predicted by Eq. (8). The high-temperature T_{1D} data reflect diffusion; values of τ_j (●) deduced from the measured T_{1D} values using Eq. (8) fit close to the solid straight line, corresponding to an activation energy $E_D = E_F + E_M = 1.33$ eV.

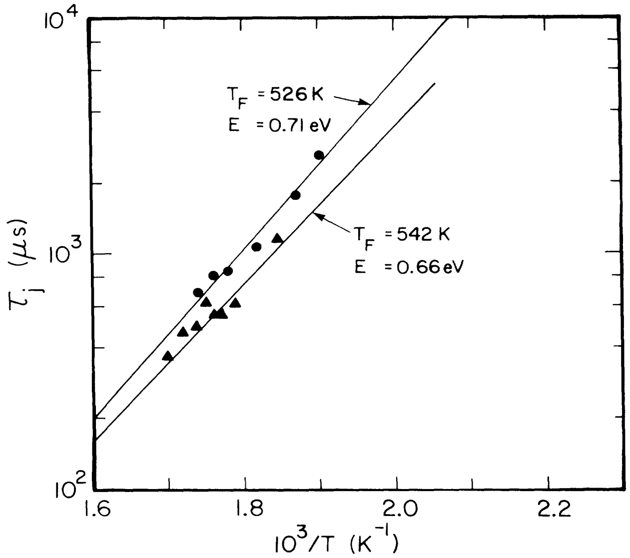

FIG. 3. Temperature-jump values of diffusion time τ_j. The τ_j were deduced from nonequilibrium T_{1D} measurements using Eq. (8). The vacancy concentration was equilibrated at 526 K (●) and 542 K (▲). Least-squares fit lines are shown along with their activation energies.

We believe the activation energies from Fig. 3 represent the vacancy migration energy E_M. Previous measurements of E_F in aluminum have been reviewed and a best value of 0.66 eV has been determined.[21] Using our value of $E_D = 1.33$ eV, the value of E_M is therefore 0.67 eV. The average of our nonequilibrium results is in good agreement with this value. The good agreement is the evidence that the measurements were indeed performed at constant vacancy concentration.

The rf heating we used was inadequate in several ways. We would have preferred larger temperature jumps $T_M - T_F$ to extend the range of the data. The heating should ideally be very rapid, certainly faster than the 0.1 s used here. This is very important for molecular solids which have high densities of dislocations.[23] If a step-function temperature change could be obtained instead of that in Fig. 1, it would be possible to measure T_{1D} after progressively longer waiting times. In this way, the experiment could observe the vacancy concentration returning to equilibrium. The observed T_{1D} could then be extrapolated back to zero waiting time and truly fixed vacancy concentration. A final shortcoming of the rf heating is that it is restricted to conductive or dielectrically lossy samples. We expect that pulsed laser heating may be the ideal solution to all of these problems.

The experiment described here involves a traditional NMR determination of diffusion on a nonequilibrium sample. The sample is heated rapidly enough with rf eddy-current heating that the vacancy concentration remains essentially unchanged. The temperature dependence of the atomic jump rate ω_j yields the vacancy migration energy E_M. The results reported here for pure aluminum foil agree well with previously reported values of E_M. This indicates that the vacancy concentration was in fact out of equilibrium during the diffusion measurement.

The method reported here demonstrates that NMR can be used to separately determine E_M and E_F $(=E_D-E_M)$. It is applicable to all kinds of materials, not just metals, provided that rapid heating and/or cooling of the sample can be arranged. Furthermore, because the NMR diffusion measurement involves microscopic distances, the measurement is not susceptable to effects from "pipes" as are macroscopic diffusion techniques.[23] The technique reported here, coupled with laser heating pulses, would be an elegant solution to measuring E_F and E_M in nearly all crystalline solids.

We are in Professor Slichter's debt for suggesting this experiment. We are grateful to Professor T. J. Rowland for a helpful conversation. The work was performed at the College of William and Mary, Department of Physics. We appreciate the generosity of the donors to the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. The work was also funded by the Jeffress Memorial Trust; one of us (M.S.C.) received support from the Alfred P. Sloan Foundation.

---

[1] N. L. Peterson, in *Solid State Physics,* edited by F. Seitz, D. Turnbull, and H. Ehrenreich (Academic, New York, 1968), Vol. 22.

[2] N. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystals* (Dover, New York, 1964).

[3] A. Seeger, D. Wolf, and H. Mehrer, Phys. Status Solidi (b) **48**, 481 (1971).

[4] R. O. Simmons and R. W. Balluffi, Phys. Rev. **117**, 52 (1960).

[5] R. Feder and A. S. Nowick, Phys. Rev. **109**, 1959 (1958).

[6] G. Bianchi, D. Mallejac, C. Janot, and G. Champier, C. R. Acad. Sci. **263**, 1404 (1966).

[7] D. L. Losee and R. O. Simmons, Phys. Rev. **172**, 934 (1968).

[8] P. Korpiun and H. J. Coufal, Phys. Status Solidi (a) **6**, 187 (1971).

[9] L. A. Schwalbe, Phys. Rev. B **14**, 1722 (1976).

[10] A. T. Macrander, Phys. Rev. B **21**, 2549 (1980).

[11] T. Federighi, in *Lattice Defects in Quenched Metals,* edited by R. M. J. Cotterill, M. Doyoma, J. J. Jackson, and M. Meshii (Academic, New York, 1965); also see other articles in the same volume.

[12] R. O. Simmons and R. W. Balluffi, Phys. Rev. **117**, 62 (1960).

[13] W. DeSorbo and D. Turnbull, Acta. Metall. **7**, 83 (1959).

[14] K. Furukawa, J. Takamura, N. Kuwana, R. Tahara, and M. Abe, J. Phys. Soc. Jpn. **41**, 1584 (1976).

[15] P. Tzanetakis, J. Hillairet, and G. Revel, Phys. Status Solidi (b) **75**, 433 (1976).

[16] E. Hashimoto, Y. Murakami, and T. Kino, J. Phys. Soc. Jpn. **49**, 1123 (1980).

[17] W. DeSorbo and D. Turnbull, Phys. Rev. **115**, 560 (1959).

[18] J. Bass, Philos. Mag. **15**, 717 (1967).

[19] R. N. West, in *Positrons in Solids,* edited by P. Hautojarvi (Springer-Verlag, New York, 1979).

[20] P. Hautojarvi and A. Vehanen, in *Positrons in Solids,* edited by P. Hautojarvi (Springer-Verlag, New York, 1979).

[21] A. Seeger, J. Phys. F **3**, 248 (1973).

[22] B. T. A. McKee, W. Triftshauser, and A. T. Stewart, Phys. Rev. Lett. **28**, 358 (1972).

[23] J. N. Sherwood, in *The Plastically Crystalline State,* edited by J. N. Sherwood (Wiley, New York, 1979).

[24] D. N. Seidman and R. W. Balluffi, Phys. Rev. **139**, 1824 (1965).

[25] K. Ono and T. Kino, J. Phys. Soc. Jpn. **44**, 875 (1978).

[26] C.-Y. Sun, Ph.D. thesis, University of Illinois, 1971 (unpublished).

[27] E. Fukushima and S. B. W. Roeder, *Experimental Pulse NMR: A Nuts and Bolts Approach* (Addison-Wesley, New York, 1981).

[28] J. Jeener and P. Broekaert, Phys. Rev. **157**, 232 (1967).

[29] C. P. Slichter and D. Ailion, Phys. Rev. **135**, 1099 (1964).

[30] D. C. Ailion, in *Advances in Magnetic Resonance,* edited by J. S. Waugh (Academic, New York, 1971), Vol. 5.

[31] C. P. Slichter, *Principles of Magnetic Resonance* (Springer-Verlag, New York, 1980).

[32] A. G. Anderson and A. G. Redfield, Phys. Rev. **116**, 583 (1959).

[33] J. J. Spokas and C. P. Slichter, Phys. Rev. **113**, 1462 (1959).

[34] F. Y. Fradin and T. J. Rowland, Appl. Phys. Lett. **11**, 207 (1967).