F^{19} nuclear Zeeman energy. In fact, the observed spectrum shows that the separation between the D_1 and A_0 lines as well as between the D_3 and A_{+1} lines corresponds to approximately twice the F^{19} nuclear Zeeman energy.

The maximum F^{19} nmr enhancement of nearly 100 obtained in this experiment is significant in view of the belief that it is one of the largest ever observed in an ionic crystal at room temperature. If one employs a higher microwave power source, a greater nuclear polarization may be obtained from the crystals. It is also interesting to note that the dynamic nuclear polarization in the crystals is obtained from second-order forbidden transitions, which appears to be very unusual.

---

*Research supported by U. S. Air Force Systems Command, Rome Air Development Center, Griffiss Air Force Base, New York.

[1] J. I. Hall and R. T. Schumacher, Phys. Rev. 127, 1892 (1962).

[2] F. N. H. Robinson, J. Sci. Instr. 36, 481 (1959).

[3] See, for example, C. D. Jeffries, Dynamic Nuclear Orientation (Interscience Publishers, Inc., New York, 1963).

[4] B. Bleaney, Phil. Mag. 42, 441 (1951).

THEORY OF "SUPERTAILS" OF IONS BOMBARDED INTO CRYSTALS

M. Sparks*
Hughes Research Laboratories, Malibu, California
(Received 19 September 1966)

When heavy ions with energies less than 1 MeV are injected into a crystal, they are stopped near the surface of the crystal—typically within a fraction of a micron.[1] But measurements[2-6] of the number of implanted ions per cm^3 have revealed large concentrations of ions much deeper (up to 10 μ) than the normal stopping region. Channeling[7] affords one explanation of penetration up to depths of ~1 μ, but the "supertails"[2] extending several microns deep are almost certainly not caused by channeling.[4] All "supertails" observed to date have either the form $(x+d)^{-\eta}$, with $\eta \cong 2$ to 7, or the form $\exp(-kx)$. Both of these forms are explained by a simple steady-state diffusion model, which was suggested independently and earlier by McCaldin.[8] Kornelsen et al.[3] also suggested that interstitial diffusion stopped by vacancies might be important. Previous explanations of these "supertails" have involved either superdeep channeling[9,10] or a single-stream diffusion with a constant number of traps.[4,11] The possibility of anomalously deep penetration due to the periodicity of the lattice has been discussed by De Wames, Hall, and Lehman,[12] and the effect of the crystal binding of target atoms on the scattering process has been considered by De Wames and Hall.[13]

The present theory affords a new method of measuring diffusion constants and binding energies of damage centers which are otherwise difficult to measure, and it offers a method of tailoring different types of concentration profiles such as $\exp(-x^2)$, $\exp(-kx)$, or $(x+d)^{-\eta}$.

Every implanted ion produces many vacancies V and self-interstitials I. We assume that the diffusion of the vacancies and self-interstitials is unaffected by the relatively small number of implanted ions (denoted by B for bombard), and that the diffusion is fast enough so that at the distances into the crystal where the observations are made, the steady state is maintained during the implanting time.[14] Then the diffusion of the V's and I's is described by the equations

$$0 = D_V(d^2n_V/dx^2) - \beta n_V n_I, \tag{1}$$

$$0 = D_I(d^2n_I/dx^2) - \beta n_V n_I, \tag{2}$$

where D's are diffusion coefficients, n's the number of V's or I's per cm^3, and the term $-\beta n_V n_I$ represents the combining of vacancies and self-interstitials. The solution of (1) and (2) determines the density $n_V(x)$ of vacancies. The interstitial B diffusion reaches its steady state also, and the interstitial B's and the vacancies combine to give substitutional B's, which diffuse so slowly that they are assumed trapped in place. After the implantation, the interstitial B's, self-interstitials, and vacancies diffuse away rapidly, leaving the substitutional B's.

The solution of the two coupled nonlinear differential equations (1) and (2) for $x > l$ is[15]

$$n_I(x) = n_I(l)\left(\frac{1-e^{-kd}}{1-e^{-k(x-l+d)}}\right)^2 e^{-k(x-l)}, \tag{3}$$

$$n_V(x) = (D_I/D_V)n_I(x) + Rn_V(l), \tag{4}$$

where

$$R \equiv \frac{D_V n_V(l) - D_I n_I(l)}{D_V n_V(l)} \tag{5}$$

and $x = l$ defines the border of the stopping region. The interesting feature of the solution (3) and (4) is that for $R = 0$,

$$n_V(x) = \frac{D_I}{D_V} n_I(x) = \frac{n_V(l) d_0^{\,2}}{(x-l+d_0)^2}, \tag{6}$$

where

$$d_0 = \left(\frac{6D_I}{\beta n_V(l)}\right)^{1/2} = \left(\frac{6D_V}{\beta n_I(l)}\right)^{1/2}, \tag{7}$$

while for $D_V n_V(l) \gg D_I n_I(l)$, i.e., for $R \cong 1$,[16]

$$n_V(x) \cong \text{constant} \equiv n_V(l),$$

$$n_I(x) \cong n_I(l) e^{-k(x-l)}. \tag{8}$$

For intermediate values of R, n_V and n_I have the form (6) for $x - l < x_c \equiv d_0/R^{1/2}$, and they have the forms (8) for $x - l > x_c$.

The number n_B of interstitial B's is determined by the steady-state diffusion equation

$$0 = D_B(d^2 n_B/dx^2) - \beta_B n_V n_B. \tag{9}$$

For n_V given by (8), the solution to (9) is

$$n_B(x) = n_B(l) \exp[-k_B(x-l)],$$

$$k_B^{\,2} \equiv \beta_B n_V(l)/D_B, \tag{10}$$

and for n_V given by (6) the solution is

$$n_B(x) = n_B(l) \frac{d_0^{\,r}}{(x-l+d_0)^r},$$

where r is the positive root of

$$r(r+1)/6 = \beta_B D_I/\beta D_B. \tag{11}$$

Finally, the number n_S of substitutional B's is, with τ the implantation time,

$$n_S(x) = \int_0^\tau dt\, \beta_B n_V n_B,$$

$$n_S(x) = \beta_B \tau n_V(l) n_B \exp[-k_B(x-l)] \tag{12a}$$

for $R \cong 1$,

$$n_S(x) = \beta_B \tau n_V(l) n_B(l) \frac{d_0^{\,2+r}}{(x-l+d_0)^{2+r}} \tag{12b}$$

for $R = 0$.

Creation and annihilation of V's and I's in pairs and particle conservation normally make $R = 0$, giving the power-law concentration (12b).[17] However, deviations from the power law are sometimes possible, as discussed in Ref. 15 and below for the experiment in Ref. 6. Other salient features of the power-law profiles are the following: The power $\eta = 2 + r$ is independent of bombarding energy E, dose rate J, and time τ, but depends on temperature T in general. The amplitude of n_S at $x = l$ is proportional to τ, and the displacement d_0 is independent of τ. The behavior of $n_S(l)$ and d_0 as functions of T, E, and J depend on the stopping profile and surface effects, but a simple model with $l = 0$ and $J = -Ddn(0)/dx$ gives $d_0 = (12D_V D_I/\beta f J)^{1/3}$ and $n_S(l) = Cf^{1/3}\tau J^{4/3}$, where C is a function of D's and β's only, and fJ is the vacancy flux. It is possible that deep in the supertail, n_S may be independent of τ if $R \neq 0$ during the latter part of the bombardment.

In Ref. 5, where 20-keV Sb ions were implanted into Si at 500°C, n_S was found to have the power-law form (12b), with $r \cong 0.2$, for over four decades of n_S and $0 < x < 10\ \mu$. Only the orders of magnitudes of the constants in (11) for r are known, but $r = 0.2$ if $D_B = 25D_I$ and $D_V \gg D_I, D_B$, for example.

Implanting 20-keV xenon into tungsten has given a "supertail"[2-4] as shown in Fig. 1, where the points from the experimental curve fit the solid theoretical curve $\sim(x-l+d_0)^{-5.7}$ very well. The poor fit to an exponential is shown for comparison. Since the residual activity is the integral of the remaining n_S's, this gives $n_S \sim(x-l+d_0)^{-6.7}$. The reasonable value of $r = 4.7$ could result from $D_V \gg D_I = 4.5D_B$, for example. Changing E from 20 to 40 keV[3] left r unchanged within the accuracy of fitting the curves, as expected from the theory. The authors' convincing argument that only interstitial B's dif-

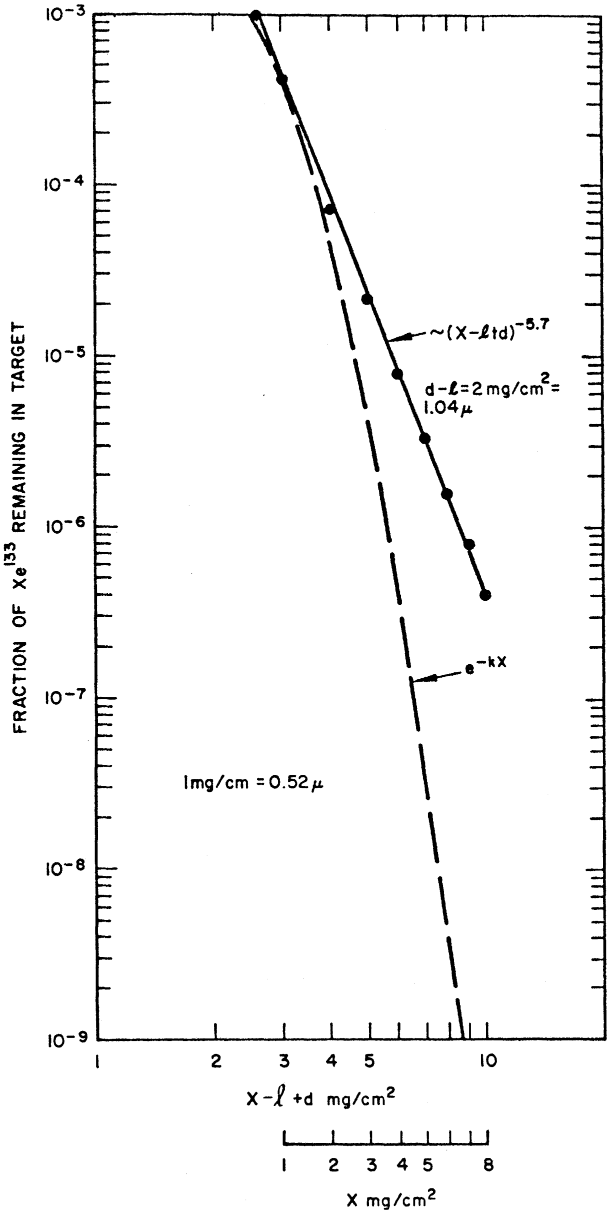

FIG. 1. Integral penetration distribution for 20-keV Xe into tungsten in the [111] direction. The points are replotted from the experimental curve of Fig. 3, Ref. 4, and the solid curve is theoretical. The dashed exponential curve, from the previous theory,[4] was fit to the slope and height of the experimental curve at $x = 1$ mg/cm² and is four orders of magnitude too small at $x = 8$ mg/cm².

fuse is in agreement with our theory. Their fixed-trapping model is quite plausible, and may dominate over the diffusing-trap mechanism in some cases.

Some profiles not extending to the usual depths of "supertails" could also possibly involve diffusion. Both Xe^{133} and Kr^{85} implanted at 5 keV into polycrystalline tungsten[3] had power-law profiles with $r = 2$ for three decades of n_S extending from very near the crystal surface to $x \cong 0.07$ and 0.14 μ, respectively (with $d_0 - l = 0.013$ mg/cm² $= 0.0067$ μ and 0.02 mg/cm² $= 0.01$ μ, respectively). Although the profiles are within the measured channeling range for aligned single crystals, the fact that two different ions have the same, and special, value of $r = 2$ suggests either $D_V \ll D_I, D_B$ or a two-stream diffusion of V's and interstitial B's.[15] At 20 keV the polycrystalline profiles appear to be more complicated.

For implantation of 5×10^{14} ion/cm² of 30- and 50-keV phosphorus ions into Si, the concentration decreased exponentially for six orders of magnitude of n_S for $0 < x < 0.5$ μ.[6] Even though 0.5 μ is within the channeling range for well-aligned beams, it seems difficult to explain six decades of exponential decrease by channeling. An alternative possibility is that since the concentration of n_S is very large ($\sim 4\times10^{21}$ cm^{-3}) in the stopping region, a substantial fraction of the interstitials created are interstitial B's rather than self-interstitials I. Since the V's and I's are therefore created at different rates, $R \neq 0$, giving the observed exponential profile (12a). Under similar experimental conditions, nitrogen implanted into Si showed no evidence of a "supertail,"[6] suggesting that the nitrogen probably diffuses slowly in Si. The relative effects of diffusion and channeling in these last two experiments is an open question.

The effects of the theory on the interpretation of other experiments, including vacancy-enhanced diffusion, will be discussed later.[15]

Interaction with R. Baron, R. W. Bower, Ramzy Mankarious, O. J. Marsh, J. Mayer, G. Picus, and G. Shifrin was invaluable in formulating the theory. J. A. Davies and R. Baron made valuable suggestions. The author gratefully acknowledges stimulating conversations with R. Kikuchi, J. Gibbons, J. Moll, and G. Pearson. W. Kleinfelder and J. Gibbons kindly allowed us to discuss their unpublished data, and J. McCaldin discussed his unpublished work freely.

---

*Present address: North American Aviation Science Center, Thousand Oaks, California. On leave of absence from Standford University, Stanford, California.

[1] J. Lindhard and M. Scharff, Phys. Rev. 124, 128 (1961). This theory, developed for gases and amor-

phous solids, has been applied successfully to crystals in the normal stopping region (excluding channeling and diffusion).

[2] B. Domeij, F. Brown, J. A. Davies, G. R. Piercy, and E. V. Kornelsen, Phys. Rev. Letters 12, 363 (1964).

[3] E. V. Kornelsen, F. Brown, J. A. Davies, B. Domeij, and G. R. Piercy, Phys. Rev. 136, A849 (1964).

[4] J. A. Davies and P. Jespersgard, Can. J. Phys. 44, 1631 (1966).

[5] R. W. Bower, R. Baron, J. W. Mayer, and O. J. Marsh, Apply. Phys. Letters 9, 203 (1966).

[6] W. Kleinfelder and J. Gibbons, private communication.

[7] See Refs. 2 and 4 for convincing channeling experiments and for references to previous channeling literature.

[8] J. O. McCaldin, private communication.

[9] C. Erginsoy, Phys. Rev. Letters 12, 366 (1964).

[10] J. O. McCaldin and J. A. Brinkman, Phys. Letters 17, 221 (1965).

[11] J. O. McCaldin, Progress in Solid-State Chemistry (Pergamon Press, New York, 1965), Vol. 2, p. 9.

[12] R. E. De Wames, W. F. Hall, and G. W. Lehman, Phys. Rev. Letters 148, 181 (1966).

[13] R. E. De Wames and W. F. Hall, Phys. Rev. Letters 17, 125 (1966).

[14] Radiation damage studies indicate that vacancies, self-interstitials, and many impurity interstitials are mobile in Si even at room temperature.

[15] M. Sparks (in preparation) gives details of the solution and the expression for d and k.

[16] If $D_I n_I(l) \gg D_V n_V(l)$, then (8) is still valid if the V and I subscripts are interchanged. All conclusions will be valid in either case.

[17] A complete argument for $R=0$ will be given in Ref. 15.

MELTING RELATIONS

Stanley E. Babb, Jr.
University of Oklahoma, Norman, Oklahoma

(Received 30 September 1966)

The announcement by Kraut and Kennedy[1] of a relationship between the melting temperature of a substance and its isothermal compression,

$$\Delta T = K_{\text{iso}} |\Delta V/V_0|_{\text{isothermal}}, \tag{1}$$

has caused a flurry of re-examinations of melting relations. Gilvarry[2] has shown how (1) can be derived from his earlier work, and more recently Vaidya and Raja Gopal[3] have published an equation,

$$\Delta T = K_{\text{m.c.}} |\Delta V/V_0|_{\text{m.c.}}, \tag{2}$$

which is nothing more than a binomial expansion of several equations appearing in the literature,[4] which are derived from the Lindemann melting relationship, and may be written in the form

$$(T/T_0) = (V_0/V)^k|_{\text{m.c.}} \tag{3}$$

It is possible to throw considerable light on the accuracy of these relations and their modes of derivation by comparison of the equations with some of the most accurate results available. In all of these equations $\Delta T = T - T_0$, $\Delta V = V - V_0$, and T_0 is the normal melting temperature of the substance. V_0 is the room-temperature solid volume in Eq. (1) and the melting-temperature solid volume in (2) and (3). The various k's are constants, and the abbreviation m.c. indicates that the volumes and volume changes so indicated are to be taken along the melting curve.

Table I shows the comparisons for the case of nitrogen, using the 65°K isotherm data of Stewart[5] coupled with the data of Grilly and Mills[6] for the melting temperatures and volumes along the melting curve. The deviations from Eq. (2) are clearly large in comparison with the experimental observations, and while the deviations from (1) are larger, it is not entirely clear that the volume data are sufficiently accurate for the comparison to be meaningful. One should note that internal precision is of more importance in checking deviations than absolute accuracy. It is also clear that the "constant" k in Eq. (3) is not constant and, in fact, the expressions given earlier by the author[4] for the variations of this quantity are not capable of reproducing its behavior accurately. The $Q(x)$ appearing in Gilvarry's expressions is close to unity for nitrogen.

For a better discussion of (1), two substances suffice. The first of these is sodium, results for which are shown in Table II. Here Bridgman's old 12-kbar measurements,[7] because of their marked superiority (a factor of about 50) in precision, which more than outweighs