

in an external magnetic field. For $t > 1$ one has in all cases $c_H \propto T^{-2}$, as is also obtained for independent spins in a magnetic field $h \ll kT$.

Results for the magnetic field dependence of $\chi(T)$ and $c_H(T)$ and for the entropy will be published elsewhere.

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³I use the notation of EA with $\tilde{J}_{ij} = J_{ij}c_i c_j$, where $c_i = 0, 1$, depending on whether a lattice site i is occupied by a magnetic atom or not. In the following i, j label impurity sites only.

⁴I assume that there is no preferred direction in spin glass for $h \rightarrow 0$, that is $\chi_{zz} = \chi_{xx} = \chi_{yy}$, and use $[H, \sum_i S_{i,\alpha}] = 0$.

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⁹Actually the application of the Feynman variation principle is complicated because of the fact that we have to go to second order in $H' = H - H_0$, where H_0 is the trial Hamiltonian, since first-order terms in \tilde{J} vanish after the \tilde{J} integrations. However, following Ref. 8 one can show that to order m

$$\text{Tr}_\alpha \exp(-\beta H_0 - \beta H')$$

$$\geq \text{Tr}_\alpha \exp(-\beta H_0)(1 - \beta H' + \frac{1}{2}\beta^2 H'^2),$$

which still remains correct if one drops in H' the term proportional to ζ^2 . After performance of the \tilde{J} integrations this leads to an expression which is analogous to the classical expression (3.13) of EA. Following EA we use the variation principle in the more restrictive form $F \approx F_0(\xi)$ and $-\beta \langle H' \rangle_0 + \frac{1}{2}\beta^2 \langle H'^2 \rangle_0 = 0$ with $\partial F_0 / \partial \xi = 0$. The constant C in Eq. (6) is then defined by the second equation which leads after performance of the \tilde{J} integrations to Eq. (7) of the text.

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Polyatomic-Ion Implantation Damage in Silicon

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We have investigated the number, N_d , of displaced lattice atoms in room-temperature implantation in Si of polyatomic-carbon-ion beams (C_n^+ and $C_{n-x}O_x^+$) for several values of n , using the backscattering-channeling-effect technique. For each ion species the same energy (8.8 keV) per carbon and the same atomic fluence and flux were used. N_d increases rapidly with increasing n , indicating that the deposited-energy density within the collision cascade is a key factor in determining how much damage is created and retained.

The use of polyatomic- (or molecular-) ion beams in ion implantation provides a simple, direct method of varying the deposited-energy density within each individual collision cascade, while maintaining constant most other cascade parameters such as ion range or cascade volume. It thus provides a powerful technique for investigating some of the mechanisms involved in radiation-damage studies: for example, the role of "energy-spike" effects as recently discussed by

Sigmund,¹ or the possible existence and magnitude of significant annealing stages during implantation.

Moore, Carter, and Tinsley² found that diatomic heavy ions (As_2^+) implanted into GaAs at room temperature produced about 30% more damage than the same number of As atoms introduced as monatomic ion species (As^+). In silicon, an even larger "molecular effect" has been observed,³ with the diatomic heavy ions (As_2^+ , Sb_2^+ , Te_2^+ ,

or Bi_2^+) producing up to 80% more damage than the corresponding atomic fluence of monatomic ions.

A logical extension of these "molecular-ion" studies is to use an element for which a whole series of polyatomic-ion beams (M_n^+) is available and thus investigate the molecular effect as a function of n . For our purpose, the carbon-ion series is an obvious choice, as polyatomic-ion beams up to at least $n=20$ are readily obtained. An additional advantage in using an ion of fairly low atomic number (such as carbon) is that previous monatomic-ion studies^{4,5} have shown that annealing effects at room temperature are much more important than with heavier ions—and hence the molecular effect might be even larger than already reported.^{2,3} Indeed, some evidence of this has already been suggested by Mueller, Rysel, and Ruge⁶ and by Gyulai⁷ in their use of BF_2^+ ions as an effective way to create an amorphous boron-implanted region in Si.

The present Letter reports an investigation of lattice disorder in Si at room temperature, using 8.8-keV C^+ , 20.5-keV CO^+ , 32.2-keV CO_2^+ , and 57-keV $\text{C}_6(\text{H}_6)^+$ ion beams. The H atoms are put in parentheses to indicate that their role in creating radiation damage is assumed to be negligible. For comparison, we have also included a much heavier monatomic ion (57-keV Ga^+), which we calculate to have almost the same cascade volume and hence the same deposited-energy density as the 57-keV $\text{C}_6(\text{H}_6)^+$ ion. We have (arbitrarily) defined the cascade volume as the volume of a spheroid whose axes are determined by the longitudinal $\langle \Delta x^2 \rangle^{1/2}$ and transverse $\langle y^2 \rangle^{1/2}$ components of the damage straggling⁸; the Ga^+ cascade volume thus calculated is $\sim 18\%$ larger than that for the $\text{C}_6(\text{H}_6)^+$ ion.

All implantations were performed at 25°C into 1.0- Ω -cm p -type $\langle 111 \rangle$ Si using the 60-keV Chalk River isotope separator. The crystals were tilted $\sim 8^\circ$ from the surface normal to minimize channeling. In order to compare the various polyatomic species under comparable conditions, the total implantation time (6.0 ± 0.5 min) and the atomic fluence [$(3.2 \pm 0.1) \times 10^{14} \text{ cm}^{-2}$] of implanted (C+O) atoms were both maintained constant. Furthermore, each ion had approximately the same energy (8.8 keV) per carbon atom. In this way, the total amount of deposited energy and also the cascade dimensions, the mean range, and the straggling of the implanted atoms are expected to be the same for all ions. (In the case of CO^+ and CO_2^+ ions this identity is not quite

true; because of their mass difference, the incident energy would be partitioned between C and O in the ratio of 11.7 keV per O atom to 8.8 keV per C atom, but the corresponding ranges, straggling, etc. are still very similar.) Two or more runs were performed for each implantation condition. These duplicate analyses agreed within 10%.

A typical set of damage spectra is shown in Fig. 1. Even though the atomic fluence was held constant, we see that the peak area and therefore the damage level increases rapidly with increasing size of the polyatomic ion.

The total number N_d of displaced atoms per implanted ion is obtained by summing the damage peak areas in the aligned backscattered spectra of Fig. 1, after normalizing to the corresponding random (nonaligned) spectrum. This technique has been fully described by Eisen.⁹ A linear dechanneling correction has been applied to account for those particles that are scattered from the aligned direction by the damage at shallower depths and subsequently backscatter from non-

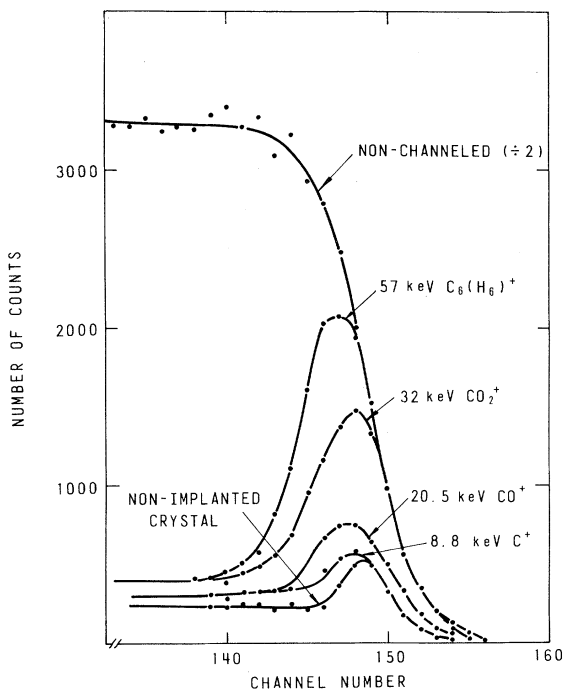


FIG. 1. Backscattering energy spectra for aligned ($\langle 111 \rangle$) and random (nonchanneled) incidence on a Si crystal implanted at room temperature with the same atomic dose [3.2×10^{14} C (and O) atoms/ cm^2] of various polyatomic ions. In each case, the ion energy was selected to correspond to 8.8 keV per C atom. The analyzing beam was 1.0-MeV helium.

displaced lattice atoms; this simplification is not serious for the shallow implants considered in the present study.

It is important to note that the damage contributing to a well-resolved peak such as those in Fig. 1 consists of grossly displaced Si atoms: i.e., individual interstitial atoms (but these are probably not stable at room temperature), clusters of interstitials, and amorphous regions. Other types of damage, such as vacancies (with their associated relaxation of neighboring lattice atoms), dislocations, or lattice strain only enhance the dechanneling rate and hence increase the scattering yield from all larger depths [see, for example, Fig. 1(A) in Pronko *et al.*¹⁰]; they do not normally produce a resolvable damage peak.

From the peak areas in Fig. 1 and from similar data for the other implants, we obtain the N_d values given in Table I. The magnitude of the molecular effect is illustrated by the ratio (N_d/n) , where n is the number of carbon plus oxygen atoms in the polyatomic ion. A strong correlation is evident between the damage per implanted atom and the size of the polyatomic ion: i.e., (N_d/n) increases more than tenfold over the range of n values in Table I. As an empirical guide, we see that (N_d/n) is nearly proportional to n^2 , indicating that, in these room-temperature carbon implants, the amount of retained damage depends roughly on the square of the deposited-energy density within the collision cascade surrounding each implanted ion.

The "straggling" mentioned above in calculating the cascade volume includes contributions both from the width of any one cascade and from the variation in shape between the different cascades. The relative importance of variation and width is difficult to estimate satisfactorily,¹¹ and hence a quantitative calculation of the deposited-energy densities for the various polyatomic ions is not possible at this stage. However, if the

calculated volume were to exclude the shape variation between cascades, then the deposited-energy density would increase more slowly than n (i.e., the average cascade volume must obviously increase somewhat as n increases), and hence the "molecular effect" reported here is an even stronger function of the deposited-energy density.

Included in Table I is the result obtained for a high- Z monatomic-ion (Ga^+) implant at the same energy (57 keV) and ion dose as the $\text{C}_6(\text{H}_6)^+$ implant. These two grossly different ion species were selected for comparison because their calculated cascade volumes (and therefore the deposited-energy densities within the individual cascades) are very similar. Strictly speaking, the collision cascade does not involve the total deposited energy, but only the nuclear-stopping portion, ν . In the present 57-keV comparison, the corresponding ν values are also very similar: viz. 37 and 34 keV for the Ga^+ and $\text{C}_6(\text{H}_6)^+$ ions, respectively. This small difference in ν values partially offsets the calculated (18%) difference in cascade volumes, so that the deposited "nuclear-energy" densities for the two cascades are almost identical—and so indeed are the observed damage levels in Table I.¹² This indicates that the concept of cascade energy density provides an effective means of correlating the lattice disorder induced in Si by various low-energy heavy ions.

An interesting extension of this work will be to investigate the magnitude of this "molecular" (or polyatomic) beam effect in Si at extremely low temperatures. Indeed, for low-energy-density cascades where thermal-spike effects are not significant,³ the presence or absence of an observable molecular effect should provide a sensitive criterion as to whether or not all annealing processes have been suppressed.

TABLE I. Values of N_d and (N_d/n) .

Ion	n	E (keV)	N_d	N_d/n
C^+	1	8.8	9	9
CO^+	2	20.5	68	34
CO_2^+	3	32.2	258	86
$\text{C}_6(\text{H}_6)^+$	6	57.0	842	140
Ga^+	1	57.0	1081	

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Nuclear Spin-Lattice Relaxation in Amorphous Materials: B_2O_3

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The temperature and frequency dependence of the nuclear spin-lattice relaxation in amorphous B_2O_3 has been investigated and a T_1 minimum with unusual properties has been discovered at ~ 300 K. The relaxation is described in detail by Raman-like processes involving the two-level disorder modes and phonons characteristic of glassy materials.

A direct comparison of the nuclear spin-lattice relaxation rates of solids in their vitreous and crystalline forms has been made in only few materials. Rubinstein and Taylor¹ studied and compared the relaxation rates of crystalline and amorphous As_2S_3 , and reported a much faster relaxation rate in the glass. Earlier, Haupt and Müller-Warmuth² found that the relaxation rate of protons in some organic glasses is much faster than in their crystalline counterparts. These results strongly indicate that defects which are intrinsic to the glassy state of matter are very effective sinks for nuclear-spin-excitation energy.

Recently Szeftel and Alloul³ examined the nuclear spin-lattice relaxation in glassy and crystalline B_2O_3 , among other samples. These authors report that T_1 (the spin-lattice relaxation time) in crystalline B_2O_3 was much longer than in glassy B_2O_3 and that the temperature dependence of the relaxation time is $T_1 \propto T^{-1.3}$ in the temperature range 1.2 to 90 K.

We report on measurements of the spin-lattice relaxation time of ^{11}B in crystalline and amorphous B_2O_3 in the temperature range 150 to 500 K, and nuclear resonance frequencies ranging from 10 to 30 MHz. We find a minimum in T_1 as a function of temperature in the vicinity of 300 K, and an increase in T_1 with increasing temperature thereafter. Our data agree with those of

Szeftel and Alloul in the small range of temperature overlap between the two experiments. Our values of T_1 are found to be practically independent of Larmor frequency ω_L at temperatures both above and below the T_1 minimum, in contrast to the predictions of the Bloembergen, Purcell, and Pound⁴ motional-narrowing theory. The temperature at which the minimum occurs is only weakly dependent on ω_L , and the value of T_1 at the minimum is nearly independent of ω_L . The measured line shape (due to random distribution of electric-field-gradient axes with respect to the applied magnetic field which broadens the ^{11}B nuclear-resonance line because of the sizable quadrupole moment of this nucleus) does not change at all in the temperature range we have covered, indicating that melting of the glass is not involved at these temperatures.⁵ We have made extensive studies of many B_2O_3 glasses containing widely different paramagnetic impurity concentrations and absorbed water content which show that the spin relaxation is unrelated to these extraneous impurities.⁶

The T_1 measurements were made on the central $-\frac{1}{2}$ to $+\frac{1}{2}$ component of the quadrupole-split resonance line with a Bruker SXP pulsed spectrometer using both the saturating-comb and the repetition-rate techniques. Both types of measurements gave identical results for T_1 . The resulting temperature dependence of T_1 in B_2O_3 is