[20] These coherency strains can also be relieved by the formation of misfit dislocations resulting in an *incoherent* crystal. However, it seems clear that such a disruption of the strong in-plane carbon-carbon bonds would severly hinder the observed (Refs. 3–5 and 11) smooth progression of stages and the reversibility of the staging process.

[21] The energy per intercalant of these distortions tends to zero as $a_0 \rightarrow \infty$.

[22] For a discussion of stage disorder and its dependence on the kinetics of intercalation, see W. Metz and D. Hohlwein, Carbon 13, 87 (1975).

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# Tunneling Modes and Local Structural Order in Amorphous Arsenic

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Pulsed nuclear-quadrupole-resonance (NQR) measurements have been performed in rhombohedral, orthorhombic, and amorphous ($a$-) arsenic. Measurements of $T_1$ provide evidence of low-frequency disorder modes in $a$-As, while the NQR frequencies indicate that the bonding is predominately $p$-like in all three materials. The asymmetric NQR line shape of $a$-As indicates that bond-angle distributions inferred from x-ray scattering and continuous–random-network models do not result primarily from a distribution in bond hydridizations.

Amorphous arsenic ($a$-As) is of interest as a prototype amorphous solid because it is an elemental material and therefore should be easier to understand than chemically more complex amorphous solids. Because all of the atoms in $a$-As are threefold coordinated, this amorphous semiconductor is structurally intermediate between the tetrahedrally coordinated group-IV amorphous films ($a$-Si and $a$-Ge) and the chalcogenide glasses, which contain group-VI elements (S, Se, and Te) in twofold coordination. All chalcogenide glasses possess anomalous low-temperature thermal properties which are a manifestation of the disorder (tunneling) modes characteristic of the amorphous phase. This behavior has not been observed in $a$-As,[1,2] which has led to the suggestion that these modes do not exist in amorphous materials which are exclusively threefold coordinated.[1,3]

In this Letter we describe $^{75}$As pulsed nuclear-quadrupole-resonance (NQR) measurements on $a$-As which provide the first evidence for disorder (tunneling) modes in this prototype group-V amorphous solid. The NQR also provides an extremely sensitive probe of $s$-$p$ hybridization of the bonding electrons in the valence band. In addition, we present the first experimental evidence of the second-nearest-neighbor angular correlations implicit in the continuous-random-network (CRN) models[4,5] of $a$-As.

There are two crystalline forms of As: the common semimetallic rhombohedral form (rh-As) and the rarer semiconducting orthorombic form (or-As). In both crystalline forms all the atoms are threefold coordinated and form six-membered rings stacked together in a layered configuration. The NQR results of these two crystalline forms provide a useful framework for the understanding of the $a$-As data.

The pulsed NQR experiments were performed using a Matec gated pulsed amplifier and receiver in conjunction with a suitably designed matching network; the spectrometer operated between 20 and 140 MHz with a bandwidth of ~1 MHz. Variable temperatures (4–300 K) were obtained with a gas (nitrogen or helium) flow system. Typical 90°–180° pulse widths employed were approximately 10–20 $\mu$sec. All observed decays were exponential, within experimental error. Samples of or-As were obtained from the Smithsonian Institution (natural mineral arsenolamprite from Chile) and A. J. Leadbetter (synthetically grown and doped with Hg). The $a$-As sample was manufactured by MCD Ltd. (99.9999% pure), while the rh-As sample (99.9999% pure) was obtained from Atomergic Chemetals Corporation.

The temperature ($T$) dependences of the spin lattice relaxation times ($T_1$) in $a$- and or-As are shown in Fig. 1. ($T_1$ versus $T$ measurements have already been reported[6] for rh-As where the relaxation is determined by the conduction electrons in the semimetal.) Below 150 K the data for $a$-As fit the relation $T_1 \propto T^{-\beta}$ with $\beta = 1.5 \pm 0.1$; similar $T$ dependences of $T_1$ for quadrupolar nuclei have been observed in all other amorphous materials studied to date ($B_2O_3$, borosilicate glass, $As_2S_3$, and $As_2Se_3$).[7,8] The dashed line in Fig. 1 represents data[9] obtained for $^{75}As$ in glassy $As_2Se_3$ where $\beta = 1.8 \pm 0.1$.

The dependences of $T_1$ shown in Fig. 1 are very weak compared to those which one observes in pure, unstrained crystalline solids, where two-phonon processes yield $T_1 \propto T^{-7}$ or $T^{-9}$ at low $T$, and $T^{-2}$ at high temperatures; likewise, relaxation due to paramagnetic impurities is much too weak for observed spin densities. This weak $T$ dependence is most likely the result of a coupling to disorder (tunneling) modes in amorphous solids.[7,8,10] Calculations of Reinecke and Ngai[10] have shown that the dominant process contributing to $T_1$ is a Raman process involving the excitation and deexcitation of tunneling modes both of which interact with the nuclear spin. If the density of tunneling modes is slowly varying with $E$ $[\rho(E) = \rho_0 E^{\eta},\ \eta < 1]$ and if the coupling to the nuclear spins is independent of energy, Reinecke and Ngai find that at low $T$

$$T_1 \propto T^{-\beta}, \quad \beta = 1 + 2\eta. \tag{1}$$

From our data (Fig. 1) we obtain a value of $\eta \simeq 0.25$ in $a$-As which may be compared to $\eta \simeq 0.4$ obtained from $^{75}As$ NQR in $As_2Se_3$ and $As_2S_3$. This result in $a$-As is surprising in view of the fact that there is to date no other evidence for the presence of tunneling modes[1-3] such as a linear term in the low-temperature specific heat or a saturating component to the ultrasonic attenuation. (These measurements are complicated by the presence of numerous cracks in bulk samples of $a$-As.) Nonetheless, the present data provide strong evidence for the existence of tunneling modes in group-V amorphous solids.

In or-As, $T_1 \propto T^{-\beta}$, where $\beta \cong 1.6 \pm 0.1$ and where the magnitude of $T_1$ is a factor of ~3 larger than in $a$-As. This behavior, which has also been observed[7] for $^{11}B$ NMR in crystalline $B_2O_3$, is a result of the imperfect and highly strained polycrystalline samples of or-As. (Both samples of or-As contained substantial amounts of $a$-As, and the natural or-As sample, arsenolamprite, contained substantial amounts of rh-As; the highly strained nature is evidenced by the broadened NQR lineshape we observe.)

The fact that the exponents in the power-law behavior of $T_1$ (Fig. 1) for $a$-As and $As_2Se_3$ (or $As_2S_3$) are different is not surprising since the relatively weak energy dependence of the densities of tunneling modes is expected to vary from material to material, particularly for two materials whose structures are as different as these. One would not, *a priori*, expect the magnitudes of $T_1$ at any given temperature to be as similar as they are for $a$-As and $As_2Se_3$. The existing models have concentrated on explaining the temperature dependence of the relaxation rates for quadrupolar nuclei in amorphous solids.[7,10] More detailed calculations with which one may compare the magnitudes of $T_1$ for different nuclei in differ-

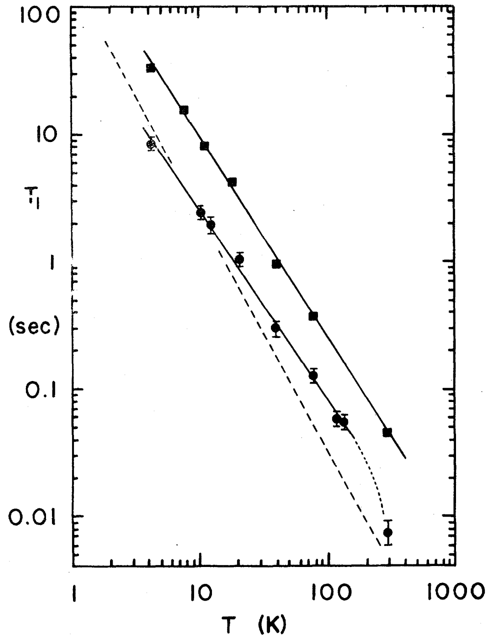

FIG. 1. Temperature dependence of $^{75}As$ NQR spin-lattice relaxation times, $T_1$, in amorphous As (circles), rhombohedral As (squares), and amorphous $As_2Se_3$ (dashed line). Solid straight lines are least-squares fits to the data.

ent amorphous solids would be most useful.

The $^{75}$As NQR absorption line shapes $a$-As and or-As are shown in Fig. 2(a). The spectrometer described above was tuned at a given frequency and the height of the spin echo was recorded after signal averaging. Relative intensities were obtained by comparison with a calibrated reference pulse. The resulting NQR frequencies at 77 K are for rh-As, 23.532 MHz[11]; for or-As, 46.3 MHz[9]; and for $a$-As ~63.5 MHz.[9] The spectrum in $a$-As is broad (~9 MHz at half-height) and asymmetric. Calculations show that the primary contribution to the NQR frequency comes from the local electronic configuration of each As atom. Since the nearest-neighbor bonding in these three forms of As is very similar even though the $^{75}$As NQR frequencies are quite different, the NQR provides a very sensitive and detailed probe of these three solids.

Experimental x-ray photoemission spectra (XPS) for rh-As and $a$-As suggest that there is very little $s$-$p$ mixing in the wave functions of the bonding electrons.[12] In fact self-consistent orthogonalized plane-wave calculations of the bonding character of many crystal wave functions in the rh-As at points of high symmetry in the Brillouin zone suggest that the $s$ admixture is on the order of 1 to 4%,[13] and tight-binding calculations for $a$-As either ignore $s$-$p$ interactions[14] or predict small $s$ admixtures.[15] The present NQR results not only are quite consistent with both of these studies, but they also provide a sensitive measure of the small $s$ admixture which is present in the electronic wave functions near the top of the valence band.

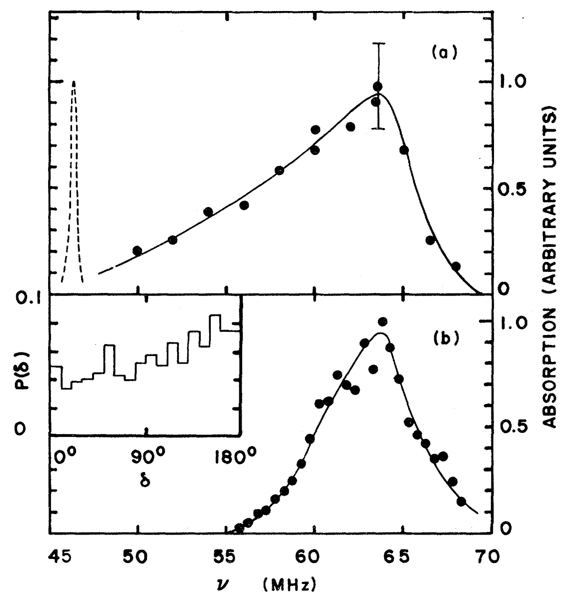

FIG. 2. (a) NQR absorption in amorphous As (circles and solid line) and rhombohedral As (dashed line) at 4.2 K. (b) Contribution to NQR line shape from bonding electrons an nearest-neighbor atoms as described in text. Inset, dihedral angle distribution from Ref. 4. The points refer to the calculated points of a histogram, while the solid line is to aid the reader's eye.

One can estimate the electric field gradient, and hence the NQR frequency, for the three forms of As from suitable tight-binding calculations. Because the differences in NQR frequencies are so great, a reasonable picture can be obtained by employing the simplest possible bond hybridization calculation (due to Townes and Dailey)[16] for the bonding electrons at an As site; we estimate the effects of the bonding electrons on nearest neighbors using hydrogenlike $4p$ orbitals parametrized[17] to fit atomic As. In all three cases, contributions to the NQR frequencies due to electrons on nearest neighbors are $\leq 3$ MHz, which represent $\lesssim 10\%$ of the total contributions. These calculations agree well with earlier results for rh-As.[18]

For the case where all three apex pyramidal hybridized bonds are identical (as in rh-As), the NQR frequency in the Townes-Dailey approximation is given by

$$\nu = \frac{Q_{cc}{}^{at}}{2} \cdot \frac{3\cos\theta}{\cos\theta - 1}\,, \tag{2}$$

where $Q_{cc}{}^{at}$ represents the coupling constant per unbalanced $p$ electron for As ($= -412$ MHz),[8] and $\theta$ is the angle between any two of the three identical hybridized bonds. If there is no $s$-$p$ hybridization, $\theta = 90°$, and $\nu = 0$ from Eq. (2). The NQR frequency for rh-As (minus ~3 MHz due to electrons on nearest neighbors) results in $\theta = 92°$ from Eq. (2) and 3% $s$ density. The difference between $\theta$ and the actual bond angles in rh-As ($\alpha = 97.1°$) reflects the complicated interplay of bond hybridization and bond overlap which would be more transparent in a detailed tight-binding calculation. For the case of or-As, an asymmetric pyramidal model was used[9]; the results indicate that the $s$ density is ~7%. For $a$-As, the predicted $s$ density is ~9%, and is very insensitive to the exact nature of the distortions which are assumed to occur. The $s$-$p$ hybridization, though weak in all cases, increases from rh-As to or-As to $a$-As. These results should encourage more realistic tight-binding calculations (such as the bond orbital[19] or cluster Bethe-lattice approaches) for or-As and $a$-As.

Additional insight into the structure of $a$-As is available from the observed NQR line shape. The continuous-random-network (CRN) models[3-5] of $a$-As utilize a distribution of pyramidal bonding angles $\sigma(\alpha)$ centered about 98° with a width at half-height of ~10°. This width cannot be due to a commensurate distribution in $s$-$p$ hybridization, since it would result in a much wider distribution of NQR frequencies than is observed. In a tight-binding picture, this width in $\sigma(\alpha)$ must be attributed primarily to a distribution in bond overlap.

Some of the width of the NQR line is possibly due to a small distribution in $s$-$p$ hybridization, but the Townes-Dailey calculations indicate that this would generate a symmetric line, such as occurs[8] in $As_2Se_3$ and $As_2S_3$. An equally important source of broadening which *does* provide an asymmetry in the observed direction is the contribution of bonding electrons on nearest-neighbor atoms. One angle uniquely defines the relative orientation of two pyramidal units which share one common bond (dihedral angle[5]). Calculations, which assumed the dihedral angle distribution $P(\delta)$ for the Greaves-Davis CRN model[4] for $a$-As [inset of Fig. 2(b)], are shown in Fig. 2(b) where the peak frequency has been scaled to match the experimental spectrum [Fig. 2(a)]. The scale on the abscissa is somewhat arbitrary because of the crude approximations employed, but the calculations do indicate that the calculated width is at least within a factor of 2 of the observed broadening. In addition, the calculated spectrum is seen to be slightly asymmetric to the low-frequency side. The asymmetry is fairly sensitive to the choice of $P(\delta)$. [A flat distribution in $P(\delta)$ yields a symmetric line.] We conclude that the NQR line shape in $a$-As is consistent with the dihedral angle distribution implicit in the CRN model.

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