Changes in the electronic structure of rhombohedral arsenic with pressure: A nuclear-quadrupole-resonance investigation

J. M. Keartland and M. J. R. Hoch
Condensed Matter Physics Research Unit, Department of Physics, University of the Witwatersrand, Johannesburg, PO Wits 2050, South Africa
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The observed nuclear spin-lattice-relaxation rate in rhombohedral arsenic may be understood in terms of nucleus-carrier and nucleus-phonon interactions. This offers the possibility of probing pressure-induced changes in the carrier and phonon properties by making relaxation measurements at high pressures. The spin-lattice-relaxation time (T_1) in arsenic (^{75}As nucleus; $I=\frac{3}{2}$) has been measured, using pulsed nuclear-quadrupole-resonance methods, as a function of pressure. The results obtained at a temperature of 295 K show that T_1 increases by approximately 25% in the range 0–9 kbar. The changes in the carrier and phonon contributions are estimated theoretically. The major contribution to the observed T_1 is thought to result from changes in the volume of the carrier pockets defined by the Fermi surface (FS). The pressure variation of the density of carrier states at the FS, $\rho(E_F,P)$, and the average effective mass, $m^*(P)$, are extracted from the data.

I. INTRODUCTION

Previous work by Keartland, Fölscher, and Hoch (KFH) (Ref. 1) has shown that the nuclear spin-lattice-relaxation time T_1 in rhombohedral arsenic gives information on the carrier and phonon properties. The extension of these measurements to pressures in the region 0–10 kbar offers the possibility of probing pressure-induced changes in these properties.

Pressure-induced changes in the carrier properties have previously been studied experimentally[2,3] and theoretically.[4] To our knowledge there have been no direct measurements of such changes in the phonon spectrum.

In this paper we report on measurements of T_1 as a function of pressure at ambient temperature. In our interpretation of the data we make several simplifying assumptions that enable us to determine the pressure variation in the density of carrier states at the Fermi level. In addition we are able to extend this analysis, by making use of the experimental data of other workers[2,5] and the calculated variation of the atomic volume with pressure.[6] We have obtained an estimate of the variation of the effective-mass parameters of the carriers with pressure.

II. THEORETICAL CONSIDERATIONS

Spin-lattice relaxation involving nucleus-carrier and nucleus-phonon interactions has been described in detail by KFH. A summary of the main ideas in that paper is presented in this section.

The spin-lattice relaxation rate for the ^{75}As nucleus ($I=\frac{3}{2}$) may be written in the form

$$\frac{1}{T_1}=6W_m+24W_{Q1}+12W_{Q2}\ , \tag{1}$$

where the quantity W_m describes magnetic interactions ($\Delta m=\pm1$) and the quantities W_{Q1}, W_{Q2} describe quadrupolar interactions ($\Delta m=\pm1,\pm2$).

Calculations of nucleus-carrier transition probabilities show that the magnetic interactions are dominated by the contact interaction, W_m^c. This may be written in terms of the carrier density of states at the Fermi level, $\rho(E_F)$, and the carrier probability density at the nucleus, $|u_k(0)|^2$. The full expression is

$$W_m^c=\frac{2\pi}{\hbar}\left[\frac{\mu_0}{4\pi}\mu_B g\mu_N\rho(E_F)|u_k(0)|^2\right]^2 kT\ , \tag{2}$$

where T is the absolute temperature and all other symbols have their usual meaning. KFH have shown that noncontact magnetic terms contribute less than 10% to the observed nucleus-carrier transition rates. Estimates of quadrupolar nucleus-carrier transition probabilities show that these terms make a smaller contribution (less than 1%).

Nucleus-phonon contributions to the observed T_1 are sizable at temperatures above the Debye temperature, Θ_D. A simple model of nucleus-phonon interactions for acoustic phonons has been outlined by Abragam.[7] The nucleus-phonon transition probabilities may be written in the form

$$W_{Q\mu}=\frac{243\pi}{16}\left[\frac{eQF_\mu\hbar}{I(2I-1)mv^2}\right]^2 \times\int_0^{\omega_D}\frac{\exp(\beta\hbar\omega)}{[\exp(\beta\hbar\omega)-1]^2}\frac{\omega^6}{\omega_D^6}d\omega\ , \tag{3}$$

where $\beta=1/kT$, μ takes the values 1 and 2, the quantities F_μ depend on the crystal structure, m is the atomic mass, v is the velocity of sound in the crystal, and ω_D is the Debye frequency ($\hbar\omega_D=k\Theta_D$). All other symbols have their usual meaning. The above expressions will be used in analyzing the experimental results.

III. EXPERIMENTAL DETAILS

The details of sample preparation and the nuclear-quadrupole-resonance (NQR) spectrometer have been described by KFH. The laboratory temperature was monitored using a thermometer and was found to remain roughly constant over long periods of time. The temperatures quoted here are accurate to 1 °C.

The high-pressure apparatus was based on the piston-cylinder method, with pressure amplification achieved in the usual way. The ram, with a maximum working pressure of 70 MPa, was served by a high-speed reversible electric pump, and the flow of hydraulic fluid into and out of the ram was controlled by a high-pressure valve. Pressure in the ram was monitored using a Heise gauge. Force from the ram was transmitted to the pressure chamber via a piston. The pressure chamber was supported by a series of pressure plates, designed to provide support and to allow passage of electrical leads into the chamber. This arrangement is a modified version of that used by Pierrus,[8] and is described in greater detail elsewhere.[9] The pressure chamber was sealed with a plug that allowed passage of electrical leads into the high-pressure cavity. A pressure gauge of 0.2-mm-diam manganin wire was placed in the sample chamber. The calibration of the manganin resistance gauge with respect to the oil pressure in the ram was accomplished using a standard method.[8] Dow Corning 200 silicone oil was used as the pressure transmitting medium.

The NQR solenoid coil was made of 0.6-mm-diam copper wire and was embedded in Stycast for rigidity. A thin-walled cylindrical sample container made of teflon was designed to allow the pressure fluid to permeate throughout the sample. After the sample was placed in the container, the powder was saturated with the pressure fluid. This had a dividend, since the fluid isolated the sample from the atmosphere and prevented oxidation.

The measurement of T_1 involves standard pulsed NQR spin-echo methods. Spin-lattice relaxation is monitored using a three-pulse sequence applied at the NQR frequency.

IV. EXPERIMENTAL RESULTS AND DISCUSSION

The relaxation data are expected to follow a relation of the form

$$1-\frac{M(t)}{M_0}=A\exp\left[-\frac{t}{T_1}\right], \tag{4}$$

where T_1 has been defined in Sec. II, $M(t)$ is the spin-echo amplitude at time t after a saturating pulse, M_0 is the equilibrium amplitude of the spin-echo, and A is a constant determined by the effect of the saturating pulse ($A\simeq 1$). T_1 is extracted from a linear regression analysis of the data obtained at high pressures. The final results are shown in Fig. 1, together with the best-fit straight line through the data. It is believed that the observed T_1 is the result of two mechanisms of similar magnitude, which are mentioned below. The slope of the line is given by

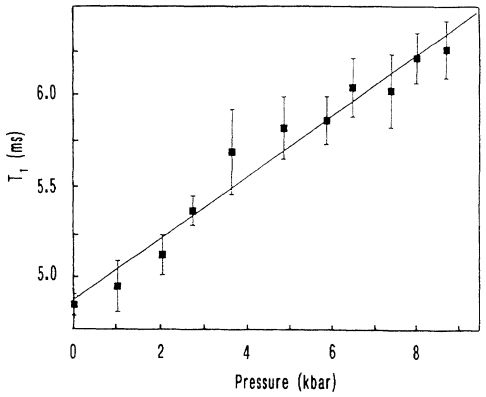

FIG. 1. Spin-lattice-relaxation time T_1 as a function of pressure. The error bars shown are the result of a linear regression analysis of the relaxation data. The curve through the data is the best-fit straight line, the slope of which is given in the text.

$$\left[\frac{\partial T_1}{\partial P}\right]_T=0.168\ \text{ms kbar}^{-1}\ . \tag{5}$$

From Fig. 1 it is clear that T_1 increases steadily with pressure. It has been shown by KFH that the observed T_1 at ambient temperature and pressure is made up of nucleus-carrier and nucleus-phonon contributions. Nucleus-carrier interactions dominate at ambient temperatures, contributing 72% of the total measured relaxation rate at atmospheric pressure. In the analysis of the high-pressure T_1 results, it is assumed that both the carrier and phonon contributions change with pressure. The pressure variation of the relaxation rate at a constant temperature may then be written as

$$\frac{1}{T_1}(P)=6W_m(P)+24W_{Q1}(P)+12W_{Q2}(P)\ . \tag{6}$$

It is assumed that the major contribution to $W_m(P)$ is due to the contact interaction, as suggested by the results and calculations of KFH. The expression for the contact magnetic interaction as a function of pressure may be written in terms of the pressure variation of the density of carrier states at the Fermi level, $\rho(E_F,P)$, as

$$W_m^c(P)=\frac{2\pi}{\hbar}\left[\frac{\mu_0}{4\pi}\mu_B g\mu_N\rho(E_F,P)|u_k(0)|^2\right]^2 kT\ . \tag{7}$$

We assume that the carrier probability density does not change significantly with pressure. This assumption is in the spirit of a first approximation and is unavoidable in the absence of good carrier wave functions for rhombohedral arsenic. The fact that the free-atom carrier wave functions approximate the crystal carrier wave functions at the nucleus (see KFH) gives us some confidence in this approximation.

Extraction of the quantity $W_m^c(P)$ from the T_1-P results will allow for the formation of the ratio

$$\frac{W_m^c(P)}{W_m^c(0)}=\left[\frac{\rho(E_F,P)}{\rho(E_F,0)}\right]^2 \tag{8}$$

and the ratio of the density of states at a pressure P to that at zero pressure may be extracted from this relation. The expression for the density of states of each carrier may be written in terms of the atomic volume v_0 and the carrier concentration n as

$$\rho(E_F) \propto v_0 n^{1/3} m^* , \tag{9}$$

where $m^* = (m_x m_y m_z)^{1/3}$. If it is assumed that the electron and hole Fermi surfaces deform uniformly and at the same rate with the application of pressure, then the ratio

$$\frac{\rho(E_F,P)}{\rho(E_F,0)} = \left[\frac{v_0(P)}{v_0(0)}\right]\left[\frac{n(P)}{n(0)}\right]^{1/3}\left[\frac{m^*(P)}{m^*(0)}\right] \tag{10}$$

may be formed for both sets of carriers. The crystal structure parameters of Morosin and Schirber[5] have been used by Hill[6] to calculate $v_0(P)/v_0(0)$, and $n(P)/n(0)$ has been measured by Brandt, Minina, and Pospelov.[2] Using these results, an estimate of the ratio $m^*(P)/m^*(0)$ may be extracted from the T_1-P data.

The changes in the (smaller) phonon contribution to the spin-lattice-relaxation rate may be estimated using some simple ideas. In this analysis only the acoustic-phonon contribution is considered. In principle it is possible to approximate the density of states of the optical phonons using the Einstein model, but the measured phonon density of states[10] shows that this would be an oversimplification. The Debye frequency may be obtained from the relation[7] $\omega_D = \sqrt{6\pi}(v/v_0)$ and the velocity of sound v may be estimated from the expression for an isotropic metal, $v = \sqrt{Y v_0/m}$, where Y is the elastic modulus, v_0 is the atomic volume, and m is the atomic mass. As an approximation it is assumed that the elastic constants do not change significantly with pressure over the range 0–10 kbar. The pressure variation of the nucleus-phonon transition probabilities may then be estimated from the ratio

$$\frac{W_Q(P)}{W_Q(0)} = \left[\frac{v(0)}{v(P)}\right]^4\left[\frac{\omega_D(0)}{\omega_D(P)}\right] = \left[\frac{v_0(0)}{v_0(P)}\right]^{3/2} \tag{11}$$

and the results of Hill[6] for $v_0(P)/v_0(0)$. This result indicates that the phonon spin-lattice-relaxation time T_1^P decreases by approximately 3.5% in the range 0–10 kbar. The nucleus-carrier spin-lattice-relaxation time T_1^C may be calculated using this result together with the experimental T_1 values and the relation

$$\frac{1}{T_1} = \frac{1}{T_1^C} + \frac{1}{T_1^P} . \tag{12}$$

The ratio $W_m^c(P)/W_m^c(0)$ may be obtained from $T_1^C(P)/T_1^C(0)$ for each pressure. This allows for the calculation of $\rho(E_F P)/\rho(E_F,0)$ using (8) and $m^*(P)/m^*(0)$ using (10) and the results of Hill.[6] These results are shown in Fig. 2. Relations of the form

$$\frac{R(P)}{R(0)} = 1 - \left[\frac{P}{P_0}\right]^{\gamma} \tag{13}$$

were fitted to each set of data, where $R(P)$ represents the relevant quantity [either $\rho(E_F,P)$ or $m^*(P)$]. The exponent γ and the fitting parameter P_0 obtained from a least-squares procedure are tabulated in Table I. These values suggest possible nonlinear behavior, but this analysis was not pursued any further in view of the scatter of the data.

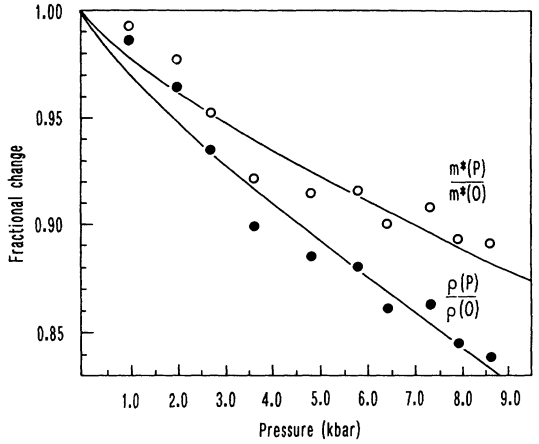

FIG. 2. Variation of $\rho(E_F,P)/\rho(E_F,0)$ (shaded symbols) and $m^*(P)/m^*(0)$ (unshaded symbols) with pressure. The data have been extracted from the results for $T_1^C(P)/T_1^C(0)$ using equations presented in the text. The curves shown are the result of a least-squares-fitting procedure described in the text. The fit parameters for each curve are tabulated in Table I.

It is appropriate at this point to consider some of the assumptions made in this analysis which have not been dealt with in the above discussion. In our discussion of the carrier contribution to T_1, we have assumed that the Fermi surfaces deform uniformly. This is clearly an oversimplification. In principle, the band-structure calculations of Pospelov[4] may be extended to calculations of the variation of the Fermi surface parameters with pressure. A calculation of $\rho(E_F,P)$ would provide a useful comparison for the results presented here.

In the discussion of the phonon contribution we have ignored the contribution of the optical phonons. While it is possible to approximate the optical-phonon density of states using the Einstein model, the measured phonon density of states[10] shows that this would be a gross oversimplification. A complete calculation would have to take into account the measured phonon spectrum. In addition, we have assumed that the lattice contributions to nucleus-phonon transition probabilities, F_μ, do not change with pressure. This is by no means clear, since

TABLE I. Parameters obtained from fitting (13) to the data shown in Fig. 3 using a least-squares procedure. These parameters suggest a nonlinear behavior of the relevant ratios with pressure.

	$\frac{\rho(E_F,P)}{\rho(E_F,0)}$	$\frac{m^*(P)}{m^*(0)}$
P_0 (kbar)	78.6	143
γ	0.81	0.77

the effects of the lattice symmetry on nuclear relaxation have not been calculated for the arsenic structure. van Kranendonk[11] has performed such a calculation for the NaCl structure.

V. CONCLUSION

The pressure dependence of T_1 at ambient temperature in arsenic has been analyzed in terms of changes in the nucleus-carrier and nucleus-phonon transition rates. The changes in the nucleus-phonon transition rates, which are smaller than the nucleus-carrier transition rate, have been estimated using a simple model. In order to study these changes more deeply, further detailed calculations of nucleus-phonon transition probabilities are required.

The variation of T_1 with pressure has provided a useful path for the investigation of carrier properties as a function of pressure. The estimates of the nucleus-phonon interactions show that they do not make a significant contribution to the observed pressure dependence of T_1 at 295 K. Estimates of changes in the density of states at the Fermi level and the average effective mass have been obtained as a function of pressure by analyzing the relaxation data. Knowledge of the crystal wave function of the carriers would aid in a more detailed analysis of the experimental results.

The NQR technique has provided useful results on changes in the Fermi surface in arsenic with pressure. These measurements should be extended to higher pressures where a minimum in the carrier concentration is observed. Band-structure calculations of the effective-mass parameters as a function of pressure have not yet been carried out, and it is not possible to compare the present results with theoretical predictions.

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