

# Pressure Dependence of the EFG in Semimetallic Arsenic and Antimony\*

G. J. Hill, J. M. Kewartland, and M. J. R. Hoch

Condensed Matter Physics Research Unit, University of the Witwatersrand, Private Bag 3, Wits 2050, Johannesburg, South Africa

Z. Naturforsch. **53a**, 501–503 (1998); received March 24, 1998

The pressure variation of the axial EFG at the ion sites in semimetallic arsenic and antimony, at ambient temperature, has been investigated using pulsed NQR. A weakly nonlinear decrease of the EFG is observed in both systems. The data are analyzed in terms of the lattice contribution to the EFG, which involves a lattice of point monopoles immersed in a uniform, compensating, background charge. The pressure dependence of the EFG obtained from the present measurements is far weaker than the pressure dependence of the calculated lattice contribution. Our results support previous suggestions that valence effects are important in determining the EFG in these semimetals.

**Key words:** EFG; NQR; Arsenic; Antimony; Pressure.

## Introduction

The group V elements, As, Sb, and Bi, crystallize in a rhombohedral structure with a two atom basis ( $A_7$  symmetry). These materials are semimetals, with small electron and hole concentrations due to band overlaps at high symmetry points in the Brillouin zone. The non-cubic symmetry of the  $A_7$  lattice leads to a substantial electric field gradient (EFG) at the nuclear sites, giving rise to a set of energy levels.

In the present paper, the pressure variation of the EFG in the semimetals As and Sb has been determined from NQR frequency measurements over the range 0–2 GPa at ambient temperature. We have carried out a preliminary analysis of the results in terms of the point charge model, which considers the EFG due to the distribution of monopole ions on the lattice.

Recent developments in electronic structure calculations employing the LAPW method [1] have been highly successful in predicting EFG's in diverse systems. The EFG's in a wide range of hcp metals have been calculated [2], and good agreement with experiment has been obtained. In these systems the EFG is dominated by non-spherical valence charge distributions near to the nucleus. TDPAD measurements of the EFG at various probe atoms in the Group V semimetals [3] suggest the local

valence electronic structure also dominates the field gradients in these systems. LAPW calculations for the Group V semimetals are planned.

## Theory

The interaction between the EFG and the nuclear quadrupole moment,  $Q$ , leads, in the axially symmetric case, to the quadrupole energy spectrum

$$E_m = \frac{e^2 q Q}{4I(2I-1)} [3m^2 - I(I+1)]. \quad (1)$$

Here  $eq$  is the component of the EFG tensor along the symmetry axis of the crystal ( $z$ -direction),  $I$  is the nuclear angular momentum quantum number, and  $m$  is the  $I_z$  quantum number. In the semimetals, the NQR frequencies lie in the rf range. The three naturally occurring isotopes used in the present work are  $^{75}\text{As}$  ( $I = 3/2$ , 100% abundant),  $^{121}\text{Sb}$  ( $I = 5/2$ , 57.25% abundant), and  $^{123}\text{Sb}$  ( $I = 7/2$ , 42.75% abundant).

The EFG is determined by the distribution of charge in the crystal. The contribution to the EFG at an ion site, chosen at the origin of the coordinate system, due to monopole ions on the lattice, is given by:

$$eq_{\text{latt}} = (1 - \gamma(\infty)) Ze \sum \frac{3 \cos^2 \theta_i - 1}{r_i^3}. \quad (2)$$

Here  $\theta_i$  and  $r_i$  are the spherical coordinates of the  $i$ 'th ion, and  $Z$  is the ionic valence. The quantity  $\gamma(\infty)$  is the Stern-

\* Presented at the XIVth International Symposium on Nuclear Quadrupole Interactions, Pisa, Italy, July 20–25, 1997.

Reprint requests to Prof. M. J. R. Hoch; Fax: +2 71 13 39 82 62.



heimer antishielding factor, which takes into account the effects of core polarization on the EFG experienced by the nucleus. The EFG given by (2) is usually referred to as the lattice contribution. We have employed the technique of Hewitt and Taylor [4] to transform (2) into a rapidly converging sum in reciprocal space.  $eq_{\text{latt}}(P)$  has been calculated for As and Sb. For As, lattice parameters were estimated by linear extrapolation of the 0–0.3 GPa X-ray diffraction data of Morosin and Schirber [5]. In Sb, lattice parameters are available over a wide pressure range [6].

### Experimental Details

Hydrostatic pressures of up to 2 GPa were achieved in a piston-cylinder apparatus. Isopentane was used as the hydrostatic medium, and pressure was measured by means of a calibrated manganin resistance gauge.

The samples were high purity (99.999%) annealed,  $\leq 20 \mu\text{m}$  powders. Fine powders are necessary for sufficient rf penetration into the metallic samples.

A coherent, pulsed NQR spectrometer, operating over the range 16–23 MHz, was used. Spin-echo methods were employed to measure the NQR frequencies of the  $3/2 \leftrightarrow 1/2$  transition of  $^{75}\text{As}$  in arsenic, and the  $5/2 \leftrightarrow 3/2$  and  $7/2 \leftrightarrow 5/2$  transitions of  $^{121}\text{Sb}$  and  $^{123}\text{Sb}$ , respectively, in antimony.

### Results and Discussion

NQR frequencies,  $\nu_Q$ , for the three transitions mentioned in the previous section, at ambient pressure, are given in Table 1. The axial EFG's in arsenic and antimony have been extracted from the NQR frequency data, using available values of the nuclear quadrupole mo-

Table 1. NQR resonance frequencies at ambient pressure and temperature for the three Group V isotopes investigated. Extracted values of the EFG in arsenic and antimony at ambient pressure are compared with the calculated lattice contribution. Values of the nuclear quadrupole moments and Sternheimer factors used are also given.

	$\nu_Q$ (MHz)	$Q$ ( $10^{-28}$ $\text{m}^2$ )	$\gamma(\infty)$	$eq_{\text{latt}}(0)$ ( $10^{21}$ V/ $\text{m}^2$ )	$eq_{\text{expt}}(0)$ ( $10^{21}$ V/ $\text{m}^2$ )
$^{75}\text{As}$ $3/2 \leftrightarrow 1/2$	22.72	0.29	-7.322	-1.4	$\pm 6.5$
$^{121}\text{Sb}$ $5/2 \leftrightarrow 3/2$	21.51	0.53	-20	-1.1	$\pm 5.6$
$^{123}\text{Sb}$ $7/2 \leftrightarrow 5/2$	19.58	0.68			

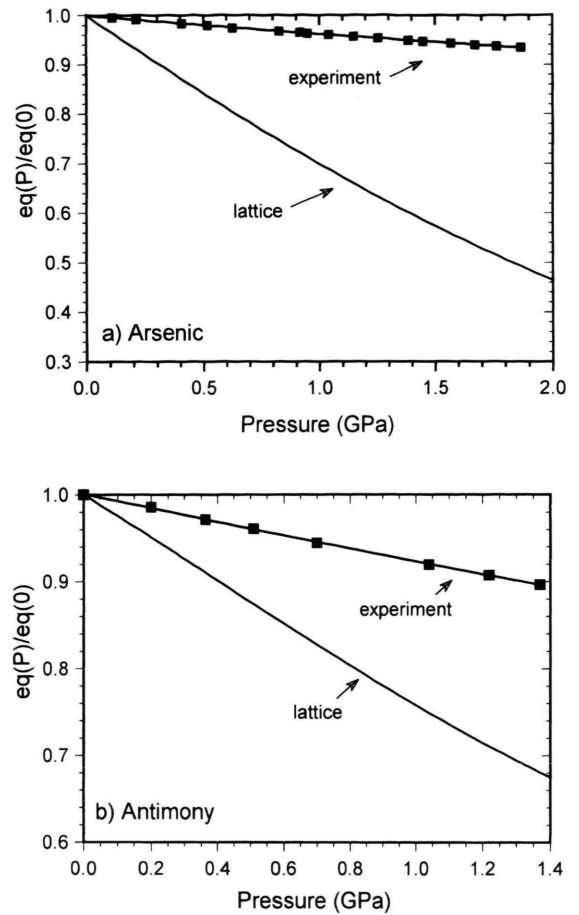


Fig. 1. Relative pressure variation of the EFG in a) arsenic, and b) antimony. The calculated variation of the lattice contribution is also shown. The lattice contribution estimated using a point charge approach amounts to approximately 20% of the measured EFG in both cases.

ments. The results,  $eq_{\text{expt}}$ , obtained at ambient pressure, are compared with the calculated lattice contribution in Table 1. We note that NQR measurements give only the magnitude, and not the sign, of the EFG. The sign of the EFG in the pure semimetals has not yet been determined conclusively. Values of the nuclear quadrupole moments and Sternheimer antishielding factors used are also given in Table 1. The Sternheimer factors used here are the results of relativistic Hartree-Fock-Slater calculations by Feiock and Johnson [7]. These authors did not give a value for Sb, and the estimate given in Table 1 is an interpolation between Feiock and Johnson's [7] values for Sb's isoelectronic ions, Sn and Te. The lattice contribution accounts for approximately 20% of the observed EFG in both arsenic and antimony.

A weakly non-linear decrease of the EFG under pressure is observed in both systems. We obtain initial slopes of  $\partial \ln eq / \partial P = -4.0 \times 10^{-2} \text{ GPa}^{-1}$  and  $-7.9 \times 10^{-2} \text{ GPa}^{-1}$  in arsenic and antimony, respectively. These results agree with previous NQR measurements carried out in these systems under moderate pressures ( $< 0.4 \text{ GPa}$ ) [8, 9].

The relative pressure variations of  $eq_{\text{expt}}$  and  $eq_{\text{latt}}$  in arsenic and antimony are shown in Figure 1. These relative variations are independent of the nuclear quadrupole moments and Sternheimer factors used, which may be unreliable. The relative pressure variation of the ionic contribution is far stronger than the experimentally observed variation of the EFG in both semimetals, indicating important valence electron effects in determining the pressure variation of the EFG.

The only published microscopic calculation of the electronic contribution to the EFG in the semimetals which we are aware of is the OAO calculation for antimony, at ambient pressure, by Hygh and Das [10]. The agreement obtained by these authors has since been considered fortuitous, in the light of modern EFG calculations, which incorporate core-shielding effects in a self consistent manner [1]. Such calculations have recently been successfully applied to the pure Group V semimetals at ambient pressure [11]. It will be of interest to com-

pare LAPW calculations of the pressure variation of the EFG with the present experimental results.

## Conclusion

Measurements of the pressure variation of the NQR frequencies in the pure semimetals, arsenic and antimony, have been extended to the wide pressure range 0–2 GPa. The axial EFG at the ion sites has been extracted using available values of the nuclear quadrupole moments. We have compared our results with the calculated magnitude and variation of the contribution due to point charges on the  $A_7$  lattice, using experimental data for the pressure variation of the lattice parameters. The lattice contribution accounts for approximately 20% of the observed EFG in both semimetals. The observed variation of the EFG, in both arsenic and antimony, is far weaker than predicted by the point charge model. As one might expect, valence electron effects appear to be important in determining both the magnitude and pressure dependence of the EFG in arsenic and antimony. The present work has made available accurate data on the nuclear quadrupole interaction in arsenic and antimony over a wide pressure range. These data should provide a useful test for modern EFG calculation techniques.

- [1] P. Blaha and K. Schwarz, *Int. J. Quantum Chem.* **XXIII**, 1535 (1983); P. Blaha, K. Schwarz, P. Sorantin, and S. B. Trickey, *Comput. Phys. Commun.* **59**, 399 (1990).
- [2] P. Blaha, K. Schwarz, and P. H. Dederichs, *Phys. Rev.* **B37**, 2792 (1988).
- [3] H.-E. Mahnke, H. Haas, W. Semmler, R. Sielemann, and W.-D. Zeitz, *Z. Phys.* **B45**, 203 (1982).
- [4] R. R. Hewitt and T. T. Taylor, *Phys. Rev.* **125**, 524 (1962).
- [5] B. Morosin and J. E. Schirber, *Sol. St. Comm.* **10**, 249, (1972).
- [6] D. Schiferl, D. T. Cromer, and J. C. Jamieson, *Acta Cryst.* **B37**, 807, (1981).
- [7] F. D. Feiock and W. R. Johnson, *Phys. Rev.* **187**, 39 (1969).
- [8] T. J. Bastow, R. J. C. Brown, and H. J. Whitfield, *Phys. Lett.* **78A**, 198 (1980).
- [9] W. J. O'Sullivan and J. E. Schirber, *J. Chem. Phys.* **41**, 2212 (1964).
- [10] E. H. Hygh and T. P. Das, *Phys. Rev.* **143**, 452 (1966).
- [11] H. Haas, private communication.