Pressure dependence of the electric-field gradient in semimetallic arsenic and antimony: NQR measurements and full-potential linearized augmented-plane-wave calculations

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The pressure variation of the electric-field gradient (efg) at nuclear sites in powder samples of semimetallic arsenic and antimony has been investigated up to 2.0 GPa at 293 K using pulsed nuclear quadrupole resonance to measure the nuclear resonance frequency. Theoretical calculations of both the total efg and the ionic contributions have been carried out. Full-potential linearized augmented plane wave (FLAPW) calculations of the total efg give values that are approximately 70% of the measured efg. The comparison between experimental and theoretical magnitudes of the efg is, however, to some extent limited by the accuracy of the values used for the quadrupole moments of ^{75}As and ^{121}Sb. Additional uncertainties arise from the pressure dependence of the lattice parameters. FLAPW calculations of the dependence of the internal z parameter on the c/a ratio suggest an inconsistency in available data for the pressure dependence of the lattice parameters. This inconsistency is particularly marked in the arsenic case, where very little high-pressure data are available. In the antimony case, our FLAPW estimate of the relative pressure variation of the efg at the nuclear sites, using experimentally determined lattice parameters, shows good agreement with the nuclear quadrupole resonance measurements. The pressure variation of the efg in arsenic is well reproduced by the FLAPW calculation when the experimental c/a ratio and theoretically estimated z parameter are used. [S0163-1829(98)03043-4]

I. INTRODUCTION

The semimetals arsenic (As) and antimony (Sb) have noncubic rhombohedral structures ($A7$ structure, $R\bar{3}m$ point group) with a substantial axially symmetric electric-field gradient (efg) at the nuclear sites. Coupling of the efg to the quadrupole moments Q of ^{75}As, and ^{121}Sb or ^{123}Sb gives rise to splittings of the nuclear energy levels that may be detected using nuclear quadrupole resonance (NQR). With knowledge of Q, the efg may be calculated from the measured NQR frequencies.

The measured efg depends sensitively on the electronic structure, with the valence charge distribution expected to make a substantial contribution. The behavior of the efg in As and Sb as a function of temperature has been inferred from previous continuous wave (cw) NQR measurements of the quadrupolar resonance frequency ν_Q. The efg in these materials varies approximately as $T^{3/2}$, as is the case in most metals.[1,2] Measurements of ν_Q as a function of pressure up to modest values (0.2 GPa in As, 0.35 GPa in Sb) have been reported for As and Sb using cw NQR.[3,4] No attempt was made in either of these previous investigations to relate the changes in ν_Q to changes in the crystal and electronic structure. In this paper, we report on measurements of ν_Q as a function of pressure up to 2.0 GPa for As and 1.4 GPa for Sb.

Changes in the crystal structure of As and Sb with pressure have been determined previously using x-ray diffraction.[5,6] It is expected that changes in the efg will result from changes in the relative positions of the core ions (which we call the lattice contribution), and from changes in the carrier or valence contribution.

In this paper we calculate the effect of pressure on the efg at the ion sites, using a self-consistent full-potential linearized augmented plane wave (FLAPW) code. In the last decade FLAPW methods, employing density functional theory, have become available for electronic structure calculations. These have been successfully applied in a wide variety of solids,[7] including metals.[8] Results of FLAPW calculations under pressure-induced variations of the As and Sb lattice parameters are presented here, and compared with the experiment. The comparison with our high precision experimental data represents a stringent test of these calculations in a complicated system.

For comparison purposes, a simple ionic approximation calculation, which ignores the valence charge distribution, has been carried out by summing over the lattice-point ions. The lattice-sum technique of Hewitt and Taylor[9] was employed. Core shielding effects are included in this ionic approximation by introducing the appropriate Sternheimer antishielding factors.[10]

The rhombohedral structure is described by the hexagonal parameters a and c, and by an internal z parameter, which gives the relative positions of the two ions in the rhombohedral unit cell. An accurate estimate of the lattice parameters is crucial for the calculation of the pressure variation of the efg. A theoretical investigation of the relationship between c/a and z has been carried out in the course of this paper, and it is found that the results differ from available x-ray diffraction data, particularly in the As case.

TABLE I. Properties of the three isotopes investigated in this work. The NQR resonance frequencies (ν_Q) and the electric-field gradients (eq) are given for ambient temperature and pressure. eq_{exp} is extracted from ν_Q using the quadrupole moment (Q) of the relevant isotope. Its sign is not known. eq_{latt} is obtained by summing over the lattice, as explained in the text, and corrected for antishielding using the Sternheimer factor (γ_∞). eq_{FLAPW} is obtained from a FLAPW calculation, as described in the text.

Isotope	ν_Q (MHz)	Q (10^{-28} m^2)	γ_∞	eq_{latt} (10^{21} V/m^2)	eq_{FLAPW} (10^{21} V/m^2)	eq_{exp} (10^{21} V/m^2)
^{75}As $\pm\frac{3}{2}\leftrightarrow\pm\frac{1}{2}$	22.720	0.29	−7.322	−1.4	−4.50	±6.5
^{121}Sb $\pm\frac{5}{2}\leftrightarrow\pm\frac{3}{2}$	21.506	0.53	−20	−1.1	−4.35	±5.6
^{123}Sb $\pm\frac{7}{2}\leftrightarrow\pm\frac{5}{2}$	19.580	0.68				

II. THEORETICAL CONSIDERATIONS

The energy levels resulting from the interaction between an axially symmetric efg, as appropriate for the lattice structure of As and Sb, and the quadrupole moment Q of a nucleus are given by

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

Here, eq is the component of the efg tensor along the axis of symmetry of the crystal, I is the nuclear angular momentum quantum number, and m is the quantum number for I_z. The energy levels are degenerate for $\pm m$. The three naturally occurring isotopes in As and Sb are ^{75}As ($I=\frac{3}{2}$, 100% abundant), ^{121}Sb ($I=\frac{5}{2}$, 57.25% abundant), and ^{123}Sb ($I=\frac{7}{2}$, 42.75% abundant). All three isotopes were studied in this paper.

The efg is determined by the distribution of charge in the crystal, and may be expected to arise from both monopole ions (lattice contribution) and the valence charge (valence contribution). The FLAPW calculation takes both of these contributions into account in a consistent way.

It is nevertheless of interest to estimate the lattice contribution to the efg at an ion site (chosen as the origin of our axis system). This may be written in terms of a sum over the lattice as

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

Here θ_i and r_i are the spherical coordinates of the ith ion and Z is the ionic valence. The quantity γ_∞ is the Sternheimer antishielding parameter, which takes into account the effects of polarization of the core electrons on the efg experienced by the nucleus. The efg given by Eq. (2) is transformed into a rapidly converging sum using the technique of Hewitt and Taylor.[9] eq_{latt} has been estimated over the pressure range studied experimentally for both 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]

The ionic approximation is expected to give crude estimates of the efg in metals, since it neglects the contribution due to the local valence electron distribution. FLAPW methods have proved to be among the most accurate charge-density calculation schemes to date. Details of the method may be found elsewhere.[7] In the FLAPW method, the charge density is determined self-consistently in the localized spin-density approximation of the density-functional theory. Hyperfine interaction parameters such as the efg can then be extracted, without making further approximations. The present FLAPW calculations have been undertaken using the WIEN95 code.[11]

Theoretical estimates of the $c/a-z$ relationship were also made using the WIEN95 code. In these calculations, the experimentally determined pressure dependence of the hexagonal parameters a and c were used, and the value of z for which the ion experiences zero force was found.

III. EXPERIMENTAL DETAILS

Hydrostatic pressures of up to 2 GPa were achieved using a piston-cylinder arrangement, which has been described elsewhere.[12] Isopentane was used as the hydrostatic medium, and pressure was measured to an accuracy of 2% by means of a calibrated manganin resistance gauge. All measurements were made at 293 K.

The samples used were high purity (99.9999%) annealed powders. Details of the sample preparation technique are given elsewhere.[13,14] A standard coherent, pulsed NQR spectrometer, operating over the range 16–23 MHz, was used to make measurements of the size of the quadrupolar spin echoes as a function of spectrometer frequency in the region of the resonance frequency. The data were fitted to a Gaussian curve, and the center of the distribution was taken as ν_Q. This method produces results for ν_Q to within an accuracy of a few kHz, in excellent agreement with those obtained using cw techniques. Measurements of ν_Q were made for the $\pm\frac{3}{2}\leftrightarrow\pm\frac{1}{2}$ transition of ^{75}As in As, the $\pm\frac{5}{2}\leftrightarrow\pm\frac{3}{2}$ transition of ^{121}Sb in Sb, and the $\pm\frac{7}{2}\leftrightarrow\pm\frac{5}{2}$ transition of ^{123}Sb in Sb.

IV. RESULTS AND DISCUSSION

NQR resonance frequencies ν_Q for the three transitions measured at ambient pressure are given in Table I. The absolute value of the axial efg (eq_{exp}) has been extracted from these results using Eq. (1), and the given values for the quadrupole moments of the nuclei (Q). These results are compared with the calculated contributions from the FLAPW results for the total efg (eq_{FLAPW}). For comparison purposes, we include our calculated lattice contribution (eq_{latt}). We note that NQR measurements give the magnitude, but not the sign, of the efg. The Sternheimer antishielding parameters, used in determining the lattice contribution, are

also given in Table I. The value used here for As is the result of Hartree-Fock-Slater calculations by Feiock and Johnson.[10] The value for Sb is an interpolation between the values of Feiock and Johnson[10] for the isoelectronic ions Sn and Te. As expected, eq_{latt} accounts for a fraction of eq_{exp} (approximately 20% in both As and Sb), assuming that the efg is negative.

Our FLAPW calculations for ambient pressure (Table I) give results that are in reasonable agreement with the measured efg in As (70%) and Sb (80%). The negative theoretical values strongly support the association of a negative sign with the experimental values. The dominant contribution to eq_{FLAPW} comes from the nonspherical local *p*-wave charge distribution, as has been found in most metallic systems.[7,8]

The correlation between the absolute values of eq_{FLAPW} and eq_{exp} obtained here for arsenic and antimony is not quite as good as has been obtained for the hcp metals.[8] This discrepancy may, however, lie in the Q values used to calculate eq_{exp}. Recent considerations suggest that the accepted values of the quadrupole moments of the semimetallic elements may be in error by up to 25%.[15]

We turn now to the pressure dependence of eq that allows us to overcome the uncertainty in Q, and provides a more stringent test for theory. The values of eq calculated by the FLAPW program depend sensitively on the lattice parameters, in particular the c/a ratio and the z parameter. The accuracy of the experimental data for these parameters as a function of pressure is quite limited. A consistent set is needed, however, for the calculation of eq. Since the experimental c/a ratios, determined from the positions of x-ray diffraction peaks, are reasonably reliable, an interpolation scheme was used to obtain a smooth pressure dependence. The experimental data for z, on the other hand, determined only from an accurate measurement of the intensity of x-ray diffraction, scatter widely.

The FLAPW procedure allows, in principle, for the calculation of all structural parameters *ab initio*. While lattice constants require absolute energy calculations, internal position parameters, such as z in the present case, may be determined from the requirement that the forces acting on the atoms in the solid vanish. It is a well-known shortcoming of the density functional approach that the resultant values of the lattice constants depend on the density functional chosen. Therefore, for c/a, the experimental data appear to be more reliable than the theoretical ones.

The opposite is true for the internal z parameter. Here, the value obtained from the FLAPW procedure at ambient pressure shows a weak dependence on the density functional, the local density approximation, and the generalized gradient approximation having been used. Furthermore, the number of k points used to represent the Fermi surface changes the resulting z parameter slightly. The calculated pressure derivative of z, however, does not depend on the approximations at all. The theoretical value for the z parameter was, therefore, considered more reliable.

The resulting pressure variation of the z parameter (z_{calc}) for As and Sb, using an interpolation of the experimental values for c and a, are shown in Figs. 1(a) and 1(b), and compared to the results obtained experimentally (z_{exp}) using x-ray diffraction. It is comforting to note that for Sb, where by far the better x-ray data are available, the theoretical z parameters are in good agreement with the experimental ones. The disagreement between z_{calc} and z_{exp} in As suggests an inconsistency in the available lattice parameter data for As. This is not surprising, since very little x-ray diffraction data for As are available. Figure 1(a) shows the linear extrapolation of the experimental result used in the present calculations. Our theoretical numbers for $z(P)$ in As lie well outside the error estimate of the initial slope of $z(P)$ given by Morosin and Schirber.[5] These results are of central importance to our problem, since the calculated values of the efg are strongly dependent on the value of z used.

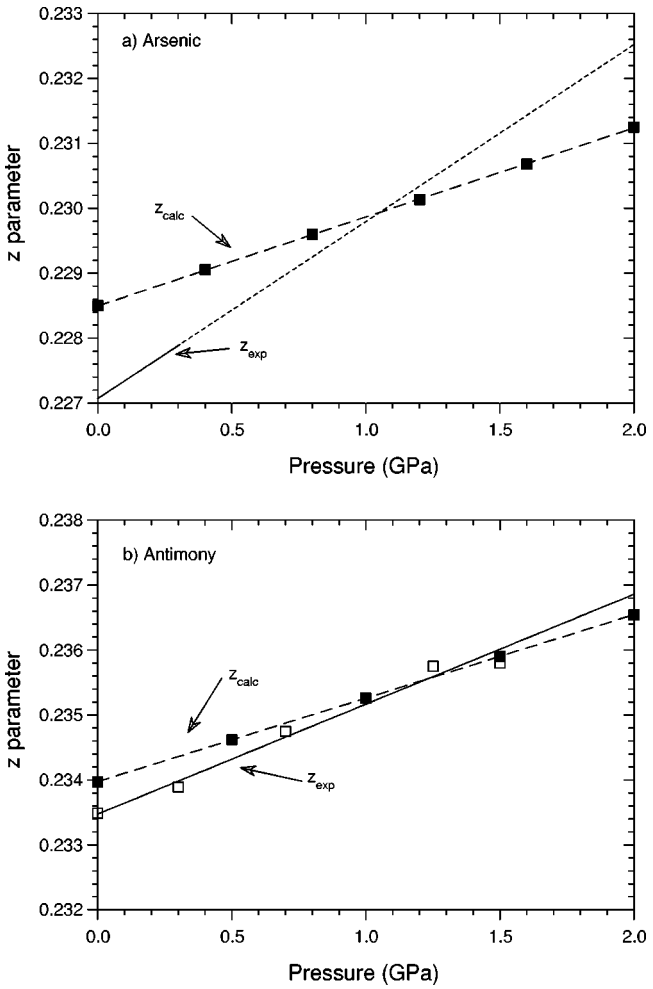

FIG. 1. (a) Pressure dependence of the z-parameter in As obtained from the results of Morosin and Schirber (Ref. 5) (solid line), the linear extrapolation of these results (short dashed line), and that obtained from zero-force FLAPW calculations assuming the experimental values for c/a (solid squares). (b) Pressure dependence of the z parameter in Sb obtained from the results of Schiferl *et al.* (Ref. 6) (open squares), and that obtained from calculation (solid squares). The calculations are described in the text.

The results of the high-pressure ν_Q measurements are summarized in Table II. The pressure dependence of eq_{exp}, relative to ambient pressure, is compared to the calculated variation of the field gradients eq_{FLAPW} and eq_{latt} in Figs. 2(a) and 2(b). In this normalized plot, uncertainties in Q are eliminated. Uncertainties in the Sternheimer factors used to calculate eq_{latt} also do not affect the comparison in Fig. 2. Calculated variations of the efg using both $z_{calc}[eq(z_{calc})]$ and $z_{exp}[eq(z_{exp})]$ are presented.

TABLE II. Measured values of ν_Q using pulsed NQR for the three isotopes investigated in this work. The experimental procedure is described in the text.

Pressure (GPa)	ν_Q (MHz)		
($\pm 2\%$)	^{75}As	^{121}Sb	^{123}Sb
ambient	22.720	21.506	19.580
0.11	22.600		
0.20		21.174	
0.21	22.520		
0.36		20.876	
0.41	22.340		
0.51		20.650	
0.52	22.250		
0.63	22.140		
0.70		20.317	18.490
0.83	21.985		
0.92	21.930		
0.95	21.890		
1.04	21.825	19.759	18.030
1.15	21.740		
1.22		19.497	
1.26	21.665		
1.37		19.261	
1.39	21.570		
1.45	21.510		
1.57	21.430		
1.67	21.358		
1.77	21.290		
1.87	21.225		

In both As and Sb, we observe a weakly nonlinear dependence of the efg, with $\partial eq/\partial P$ decreasing with increasing pressure. A decrease in the efg is expected, as the lattice tends toward cubic symmetry under pressure. The calculated variations of the efg show a qualitatively similar decrease to that observed experimentally. The curves given in Fig. 2 are second order polynomial fits to the experimental and calculated data.

The lattice contribution overestimates the observed pressure variation of the efg in both As and Sb. This indicates the importance of the valence charge in determining the pressure variation of the efg. The sensitivity of the lattice sum to the lattice parameters is demonstrated by the large difference between $eq_{latt}(z_{calc})$ and $eq_{latt}(z_{exp})$. This difference is greater in the case of As [Fig. 2(a)], where the difference between $z_{calc}(P)$ and $z_{exp}(P)$ is large.

The FLAPW results show a similar sensitive dependence on the lattice parameters used. In As [Fig. 2(a)], $eq_{FLAPW}(z_{calc})$ gives good agreement with experiment, while $eq_{FLAPW}(z_{exp})$ strongly overestimates the observed variation. In the case of Sb [Fig. 2(b)], both $eq_{FLAPW}(z_{calc})$ and $eq_{FLAPW}(z_{exp})$ give good agreement with the experiment. While the pressure dependence of the lattice parameters in As needs to be investigated further, it appears that the FLAPW method successfully describes the pressure variation of the efg in semimetallic As and Sb.

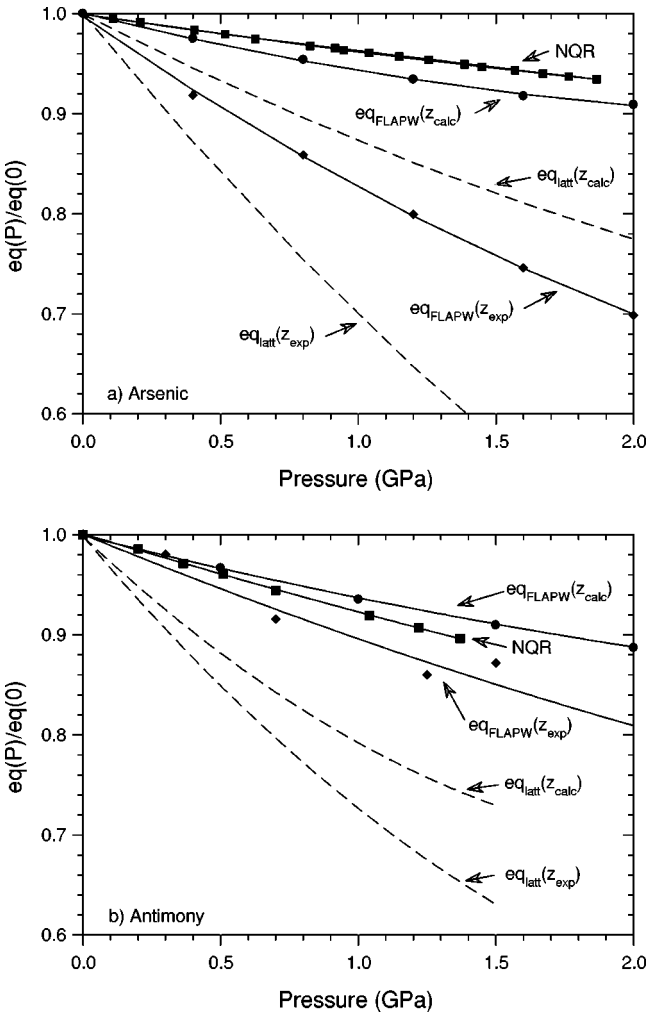

FIG. 2. Relative pressure variation of eq_{exp} (squares), eq_{FLAPW} using z_{calc} (circles), and eq_{FLAPW} using z_{exp} (diamonds) for (a) As and (b) Sb. The FLAPW result obtained using z_{calc} gives good agreement with experiment in both As and Sb. The use of z_{exp} in the As case leads to overestimates of the observed pressure variation. For comparison purposes, the lattice contributions obtained using both z_{exp} and z_{calc} are shown (dashed lines). In both cases, the lattice contribution shows a stronger pressure dependence of the efg than the experimental and FLAPW results.

V. CONCLUSIONS

The pressure variation of the efg in As and Sb has been determined by pulsed NQR measurements. FLAPW and ionic sum calculations of the efg have been performed for comparison. The experimental and FLAPW values at ambient pressure agree to within 30%. This comparison, however, is limited by the accuracy of the quadrupole moments used in determining the experimental efg. Also, the $c/a-z$ relationship as a function of pressure has been investigated theoretically.

In Sb the FLAPW calculations are consistent with experimentally observed variations of both the efg and the lattice parameters. For As, however, the experimental $c/a-z$ relationship is in disagreement with the theoretical result, and leads to overestimates of the pressure variation of the efg. Here, the use of theoretical estimates of z, assuming the experimental c/a ratio, leads to improved agreement between

the FLAPW calculations of the efg and the values extracted from NQR measurements. We have suggested that the available z parameter data for As are unreliable. Further x-ray measurements in As, covering a wider pressure range, are clearly required in order to confirm this conclusion.

The comparison of the present NQR measurements of the pressure variation of the efg in semimetallic As and Sb with FLAPW estimates provides a further test of the accuracy of the method when applied to electronically complicated systems.

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