The changes in force constants, polarization, and effective charge are large enough to have significant effect on the frequencies of defect modes. Unfortunately it would be extremely complicated to take these changes into account.

CONCLUSIONS

For wave vectors directed along axes of symmetry in the perfect rock-salt structure, the lattice-vibration waves are either purely transverse or purely longitudinal. For directions of somewhat lower symmetry, viz., when either one component of the wavevector is zero or two of them are equal, there is a pair of transverse waves. But for all other wave vectors, the waves are neither transverse nor longitudinal.

When isotopic impurities are introduced in the rock-salt lattice, local modes will appear above the optical branches for mass difference beyond a certain critical value.

Evidently it is inadequate to treat U centers in KCl and NaCl as simple isotopic impurities harmonically coupled to the lattice, without considering changes in force constants, polarization, and effective charge.

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Pressure Dependence of the Electric Field Gradient in Metallic Indium*

W. J. O'Sullivan and J. E. Schirber
Sandia Laboratory, Albuquerque, New Mexico
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The shift of the $^{115}In_{|7/2|\leftrightarrow|9/2|}$ nuclear quadrupole resonance (NQR) in indium metal has been measured at 25.5°C as a function of hydrostatic pressure to 8 kbar. In addition, the linear compressibilities at 25.5°C and the linear thermal-expansion coefficients and resonance-frequency temperature dependence in the room-temperature region were measured. Since the electric field gradient is a function of three variables, these measurements are insufficient to separate the explicit dependences. The obvious third experiment, the effect of uniaxial stress on the NQR, is not feasible, as it would require detection of the broad NQR of indium in the skin depth of a single crystal. We can therefore only infer that the major contribution to the change in field gradient is due to the change in distortion parameter $(c/a)-1$. A possible solution to this problem at one temperature is discussed.

I. INTRODUCTION

THE conduction-band contribution should be the major source of the nuclear-site electric field gradient (EFG) in metals which have noncubic structures and whose conduction bands evidence an appreciable degree of p-electron character. To date, nuclear quadrupole resonance NQR techniques have been applied to gallium[1,2] and indium [3–6] (two s- and one p-valence electron/atom) and antimony[7,8] ($5s^2\,5p^3$) in an effort to assess the importance of the conduction electrons as a source of the EFG in metals.

In principle, information relating to the conduction-electron distribution could be extracted from a model which satisfactorily represents the EFG at the nuclear site in a metal. However, it is necessary that the criteria used to assess the merit of a model be detailed enough to be significant. A comparison between a theoretical value for the EFG and the experimental value at a single temperature and pressure is insufficient. We have therefore measured the effect of pressure on the NQR, the linear compressibilities, and the linear thermal expansivities in metallic indium, in order to enlarge the set of available criteria which may be used to check theoretical models of the electron-charge distribution in indium. Indium was chosen for this investigation because of its relatively simple structure and because there has been considerable interest in the fact that its quadrupole coupling parameter is extremely sensitive to temperature change.[9]

The indium lattice is most simply viewed as a fcc

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structure with a slight tetragonal distortion along the c axis. The degree of distortion from cubic will be characterized by the parameter $\delta \equiv (c/a)-1 (\delta \sim 0.076$ at 20°C). Thus, the EFG at a lattice site in indium has axial symmetry and the observed NQR frequencies are describable in terms of eq, the field gradient component along the c axis. Even in as simple a system as indium, a minimum of three independent parameters are necessary to describe the field gradient. We choose to describe q as an explicit function of temperature, volume, and the distortion parameter, i.e.,

$$q=q(T,V,\delta). \tag{1}$$

The temperature and pressure dependences, in conjunction with the linear expansivities and compressibilities, provide only two of the three experiments necessary to separate the dependences of the EFG upon these three variables. The logical third experiment would be a measurement of the effect of uniaxial stress upon the EFG. This experiment however would require the detection of the very broad In NQR in the skin depth region of an oriented single crystal and is therefore not feasible at this time.

Since we have only two equations and three unknowns, we are able to do no more than infer that the major contribution to change in field gradient is due to the change of the distortion parameter. This problem is even more complex for gallium and metals with the arsenic-type structure as the electric field gradient is then a function of four variables. A possible solution to this problem for In is discussed in the final section.

II. PRESSURE DEPENDENCE OF THE EFG IN INDIUM

Since the EFG at a nucleus in indium metal has axial symmetry about the c axis, and this symmetry is invariant under the application of a uniform stress, the expression relating the quadrupolar coupling parameter to the frequency of a given NQR transition when pressure is applied hydrostatically to the sample is

$$\nu(P)_{|m|\rightarrow|m|+1}=[3(2|m|+1)/4I(2I-1)]e^2Qq(P)/h. \tag{2}$$

The shift in the $^{115}\mathrm{In}_{|7/2|\leftrightarrow|9/2|}$ pure quadrupole transition was determined as a function of pressure from P^0 to 8 kbar (throughout this paper P^0 will symbolize ambient pressure) at 25.5°C. All NQR measurements were carried out with a super-regenerative spectrometer system incorporating sine-wave magnetic-field modulation at 200 cps with a modulation amplitude of 35 G and phase-sensitive detection at twice the modulation frequency. Since the oscillator frequency during super-regenerative operation normally differs by 30–50 kc/sec from that in cw operation, a communications receiver was used to monitor the oscillator frequency as the detector was driven through resonance.

A superregenerative detector was used because of the sensitivity advantage it holds over a marginal oscillator when detection of broad NMR is required.[10] In the case of the ^{115}In NQR, it was not possible to separate the neighboring sidebands completely from the central resonance at quench rates as high as 100 kc/sec. As a result, the accuracy of the determination of the central resonance frequency was limited to within ±15 kc/sec. Despite this degree of uncertainty concerning the position of the central resonance, the value of the frequency shift with either pressure or temperature could be determined much more precisely. The shift in frequency for a given change in pressure was determined by measuring the frequency at characteristic points of the resonance pattern and subtracting from these the frequencies of their image points on the P^0 resonance. In all cases at 25.5°C, scatter and reproducibility were within ±8 kc/sec, at pressures up to 3.6 kbar.

The samples consisted of 99.999% pure indium powder, sifted through a 325 mesh screen into a pool of kerosene, the pressure transmitting fluid. In this way, a satisfactory suspension of the indium particles in the pressure fluid was assured.

Two pressure systems were used in the measurement of the ^{115}In NQR pressure dependence. The first, a portable stainless-steel bomb with a 4-in.×1-in. i.d. cylindrical pressure chamber, was employed for the measurements to 3.6 kbar. The pressure within this system was measured by a 0–100 000 psi Heise gauge, calibrated to ±100 psi. The second consisted of a Harwood pressure system operable to 8 kbar. The pressure within this system was measured by a bulk-modulus gauge accurate to ±500 psi. The temperature was monitored by a thermocouple placed in close proximity to the sample. Through careful pressure cycling it was possible to reduce the scatter of the temperature at which the data to 3.6 kbar were taken to ±0.2°C about the initial temperature for any given run. The temperature scatter using the Harwood machine was roughly ±1°C. The frequency deviations introduced into the data above 4 kbar by the temperature scatter were reduced to some degree by adjusting the results to the temperature at the initiation of each run using our measured $(d\nu/dT)_{P^0}=12.65\pm0.20$ kc/sec°C (valid through the range 0–30°C). In all cases, the resonances were observed both as the pressure was increased and decreased with no detectable difference in frequency at a given pressure and temperature.

The results of the measurement of the pressure dependence of the ^{115}In NQR at 25.5°C are plotted in Fig. 1. The shift of the resonance with pressure is toward increasing frequency and is roughly linear to 4 kbar, with a slope of 66.5±2 kc/sec kbar. There was no evidence of broadening or line-shape variation of the

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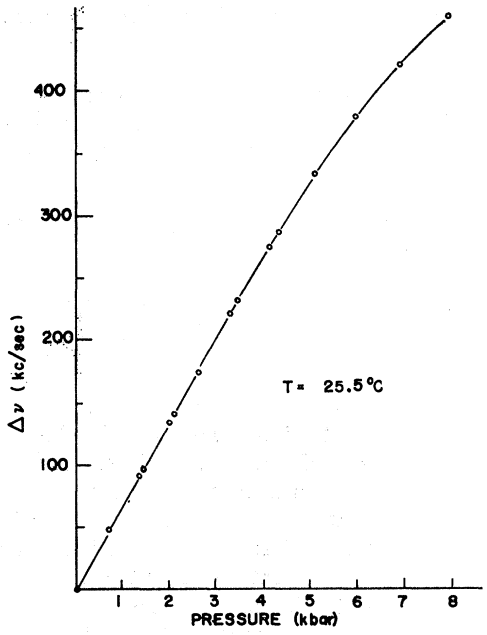

FIG. 1. The shift of the $^{115}In_{|7/2|\leftrightarrow|9/2|}$ NQR as a function of hydrostatic pressure at 25.5°C.

resonance pattern within the pressure range investigated.

III. LINEAR COMPRESSIBILITIES AND THERMAL EXPANSIVITIES

It is important to recognize that accurate values for the linear compressibilities and linear thermal-expansion coefficients for indium in the room-temperature region are required. Although the values of the lattice parameters in indium determined for a series of temperatures by Graham, Raynor, and Moore[11] are quoted to within $\pm 0.05\%$, this error corresponds to an uncertainty in δ of $\pm 1.5\%$ which in turn is roughly equal to the entire shift of δ with pressure to 3 kbar. Although the bulk compressibility of indium is very well known,[12] the linear compressibilities are not available; probably because, for most purposes, In can be considered cubic. A conservative estimate of the uncertainty which results if one attempts to use elastic constant data[13] to obtain $d\delta/dP$ is $\pm 30\%$.

Two cylindrical indium single crystals roughly 2 in. $\times\frac{1}{8}$ in. in diameter were grown. The cylinder axis of one was within 3° of the c axis and that of the second within 3° of the a axis. The growth axes of the two crystals were mutually orthogonal to within $\frac{1}{2}$°.

The variations in length of the samples with changes in pressure or temperature were detected using a combination consisting of a linear variable differential transformer (LVDT) and a mutual inductance bridge.[14] The sample was contained in a 6-in.$\times\frac{3}{8}$-in. o.d.$\times\frac{1}{8}$-in. i.d. stainless-steel pressure bomb for the compressibility measurements and in a 6-in.$\times\frac{3}{8}$-in. o.d.$\times\frac{1}{8}$-in. i.d. thin-walled stainless-steel Dewar for the thermal expansion measurements

The variation with temperature or pressure of the position of a $\frac{1}{8}$-in. steel ball bearing resting on top of the sample was detected and related to the $(\Delta l/l)$ of the 2-in.-long indium samples. The system was calibrated by a micrometer which was clamped rigidly to the sample container and on which the transformer coil rested. The calibration process consisted of moving the LVDT in 0.005 in. steps with the micrometer and reading the corresponding position of the bridge null point. The minimum detectable $(\Delta l/l)$ with this system was $\simeq\pm 5\times 10^{-6}$. Variation of the calibration over the total range of Δl was less than $\pm 1\%$.

Since we are concerned only with $\Delta(c/a)/(c/a) = (\Delta c/c) - (\Delta a/a)$ as a function of pressure and temperature, corrections to $\Delta l/l$ due to the variations in dimension of the pressure bomb and ball bearing in the former and of the dewar and bearing in the latter case are completely cancelled, if the samples are of equal length. However, it was possible to reduce these corrections to $\Delta l/l$ to the point that accurate values of the lattice parameter variations with pressure and temperature could be extracted. If the micrometer clamp is fixed to the sample holder (pressure bomb or Dewar) at a point which corresponds to the position at which the bottom of the sample contacts the container, as the container lengthens or shortens, the transformer coil which rides on the micrometer follows the variations in container length and reads only the change in dimension of the sample plus bearing.

The results of these measurements for indium are

$$\left(\frac{d\ln c/a}{dT}\right)_{P^0} = -(5.65\pm 0.20)\times 10^{-5}/^0\text{C}$$ (T varied from 0 to 40°C)

and

$$\left(\frac{d\ln c/a}{dP}\right)_{T=25.5^\circ\text{C}} = (3.60\pm 0.10)\times 10^{-4}/\text{kbar}$$ (pressure varied from P^0 to 3 kbar).

We find agreement to within 5% of the quoted volume compressibility of indium,[12] using our measured $(d\ln a/dP)_T$ and $(d\ln c/dP)_T$. It is of interest to note that $(d\ln c/dT)_{P^0}$ was determined to be $(0.00\pm 0.15)\times 10^{-5}$/°C from 0 to 30°C. The indicated errors represent the limits within which reproducibility was maintained.

IV. DISCUSSION OF RESULTS

The results of our measurements are summarized below. The values of the indium c and a lattice param-

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eters at 20°C listed in the international tables[15] and the $|\frac{7}{2}\leftrightarrow\frac{9}{2}|$ transition frequencies at 300°K quoted by Hewitt and Taylor[6] were considered exact. Our measured dependences of the lattice parameters and the frequency were then used to normalize the quantities to 25.5°C and to form the following logarithmic derivatives:

$$(d\ln q/dT)_{P0}=-(2.53\pm0.04)\times10^{-3}/°\mathrm{C},$$
$$(d\ln q/dP)_{T}=(1.33\pm0.04)\times10^{-2}/\mathrm{kbar},$$
$$(d\ln\delta/dT)_{P0}=-(8.05\pm0.25)\times10^{-4}/°\mathrm{C}\text{ and}$$
$$(d\ln\delta/dP)_{T}=(5.13\pm0.15)\times10^{-3}/\mathrm{kbar}.$$

From these results, it is seen that, at 25.5°C, a decrease of 5.25°C has the same effect on the EFG as 1.0 kbar. This temperature decrease reduces the volume by 0.059% while 1 kbar reduces it by 0.27%. On the other hand, the increases in δ with the 5.25°C temperature reduction and with 1 kbar are 0.42 and 0.51%, respectively. The inference that the EFG is more strongly correlated with changes in δ than with changes in V is obvious.

It is, however, impossible with the measurements made thus far to separate the explicit dependences of q upon T, V, and δ. A third measurement is required. The obvious experiment would be to determine the dependence of the NQR upon uniaxial stress applied to an oriented single crystal of indium. The broad In NQR is difficult to detect even in fine powder samples. The possibility of observing the resonance in the skin depth of single crystals is remote.

It is possible that a fortuitous match of the various derivatives will allow one to determine the explicit temperature dependence at one temperature which we will call T_0. This in turn allows the determination of the explicit δ and V dependences at this temperature. For this to occur we require the values of δ and V to be the same at two temperatures. Then, any difference in the NQR frequency is due to the explicit temperature dependence. This is expressed in terms of measurable quantities as

$$\left(\frac{d\ln V}{dP}\right)_{T_0}\Big/\left(\frac{d\ln\delta}{dP}\right)_{T_0}=\left(\frac{d\ln V}{dT}\right)_{P0}\Big/\left(\frac{d\ln\delta}{dT}\right)_{P0}\equiv\alpha. \tag{4}$$

With a little algebra, α can be expressed in terms of the thermal expansivities as

$$\left(\frac{d\ln c}{dT}\right)_{P0}=\frac{2\delta+(\delta+1)\alpha}{(\delta+1)\alpha-\delta}\left(\frac{d\ln a}{dT}\right)_{P0}. \tag{5}$$

Using our measured compressibilities, the room-temperature value for δ and the values for the temperature dependence of the thermal expansivities of Graham *et al.*,[11] we can make a rough calculation for the temperature T_0 at which Eq. (4) will be valid. We obtain a value for T_0 of about 130°K so it is very probable that such a temperature exists for In. In order to actually carry out this analysis, one must obtain precision values for the compressibilities and expansivities near T_0 as the remarks made in Sec. III concerning the x-ray and elastic-constant data are even more applicable at low temperatures. With these new data, T_0 can be accurately determined and the resonance experiments repeated at this temperature.

It is improbable that such a fortuitous combination of dependences will occur in either gallium or in metals of the arsenic structure (Bi, Sb, As), because in these metals, a description of the EFG requires *four* independent parameters.

It would seem that the completion of such a program as outlined above would be most worthwhile in the case of indium.

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