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Linear Stark Splitting of Nuclear Spin Levels in GaAs†

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A quadrupole splitting of the fourfold-degenerate nuclear spin levels of Ga^{69}, Ga^{71}, and As^{75} in a single crystal of GaAs has been induced by the application of a dc electric field along the [111] direction. The splitting of the nuclear magnetic resonance has been observed and the coupling constants R_{14} between the induced gradient tensor and the applied homogeneous electric field have been determined. The results are $R_{14}(Ga^{69})=1.05\times10^{10}$ cm^{-1}, $R_{14}(Ga^{71})=0.9\times10^{10}$ cm^{-1}, and $R_{14}(As^{75})=1.55\times10^{10}$ cm^{-1}. A simple theoretical model explains the physical origin of this effect quite well.

I. INTRODUCTION

THE effect of an applied electric field in magnetic resonance spectroscopy was discovered first in pure nuclear quadrupole resonance spectra.[1,2] In general, there will be a linear variation of the nuclear quadrupole coupling with electric field, whenever the nucleus is at a site which lacks inversion symmetry. It was already pointed out in the early communication[2] that sites of tetrahedral symmetry, $T_d=\bar{4}3m$, provide the interesting situation in which the electric field induces a quadrupole splitting. In the absence of electric and magnetic fields the nuclear spin level is $2I+1$ times degenerate in this cubic symmetry. If an electric field is applied, this degeneracy is at least partially lifted. In GaAs all three nuclides Ga^{69}, Ga^{71}, and As^{75} have spin $I=\frac{3}{2}$ and are at sites with $\bar{4}3m$ symmetry. If an electric field is applied, the fourfold degenerate spin level is split into two Kramers doublets.

This effect is observable by nuclear magnetic resonance (NMR) in an external magnetic field H_0. Without electric field a single resonance line is observed corresponding to transitions between four equally spaced levels. The application of an electric field splits this line into a triplet. The induced quadrupole interaction is described by

$$\mathcal{H}_{Q,E}=-\frac{e^2Q}{6I(2I-1)}\times\sum_{ij}\left[\tfrac{3}{2}(I_iI_j+I_jI_i)-\delta_{ij}I(I+1)\right]q_{ij}^E. \quad (1)$$

A matrix element of the induced field gradient tensor at the nucleus is given by

$$eq_{ij}^E=\sum_k R_{ijk}E_k+\sum\sum_{lmk} S_{ijlm}d_{lmk}E_k. \quad (2)$$

The last term represents the gradient produced by the piezoelectric strain. The first term represents the gradient produced by the electric field at constant strain. The summation indices run over the three coordinates $x=1$, $y=2$, $z=3$. If the Voigt notation $yz\equiv4$, $zx\equiv5$, $xy\equiv6$, is introduced, the only nonvanishing elements for the third order tensor in T_d symmetry are $R_{14}=R_{25}=R_{36}$. The only nonvanishing elements of the fourth order tensor are $S_{11}=S_{22}=S_{33}$, $S_{12}=S_{21}=S_{13}=S_{31}=S_{23}=S_{32}=-\frac{1}{2}S_{11}$ and $S_{44}=S_{55}=S_{66}$. The piezoelectric tensor has the same properties as the R tensor, because the crystal as a whole has the same T_d symmetry as the individual nuclear sites.

If the electric field $\mathbf{E}$ is applied along the [111] body diagonal, an axially symmetric field gradient is induced along this direction which shall be denoted by ζ. From the known transformation properties of third-order tensors one obtains immediately $R_{\zeta\zeta\zeta}=(2/3^{1/2})R_{14}$, etc. The electric field gradient is, therefore,

$$-\partial^2V/\partial\zeta^2=eq_{111}=(\tfrac{2}{3})^{1/2}(R_{14}+d_{14}S_{44})E_{111}. \quad (3)$$

In the following section the experiments will be described that lead to a determination of the phenomenological constant R_{14} for each isotope in GaAs. Although the same effect would, in principle, occur in all III–V and other compounds which crystallize in the cubic ZnS structure and have nuclear spins $I\geq1$, GaAs represents a judicious choice. It is available in a highly resistive form with almost perfect compensation of charge carriers, so that large electric fields can be applied to the sample without deleterious heating effects, depolarization or breakdown. Furthermore, the indirect spin-exchange interaction is rather smaller than for heavier isotopes. The nuclear resonance is, therefore, relatively narrow. The electric quadrupole moments are reasonably large. Therefore, the splitting induced by an applied electric field can be made larger than the linewidth and becomes thus observable.

In Sec. III a microscopic theory of the linear electric field effect is given on the basis of an oversimplified model for the valence orbitals. Reasonable agreement with the experimentally observed values is obtained. The relative simplicity of the experimental and theoretical situation was a strong motivation to study this case of T_d symmetry. The thermodynamic inverse effect, in which an electric polarization is produced as a result of nuclear spin transitions, is described in the Appendix.

An abbreviated account of this work was presented

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[1] T. Kushida and K. Saiki, Phys. Rev. Letters 7, 9 (1961).

[2] J. Armstrong, N. Bloembergen, and D. Gill, Phys. Rev. Letters 7, 11 (1961).

TABLE I. Data for electric shift of the magnetic resonance in GaAs. $\Delta\nu_E$ is the splitting between each satellite and the central component, if the electric field and magnetic field are applied along [111]. The value of R_{14} is deduced from $\Delta\nu_E$ with Eq. (4).

Isotope	NMR frequency at 10^4 Oe (Mc/sec)	$Q\times10^{24}$ (cm^2)	$\Delta\nu_E$ in kc/sec for 10^4 V/cm	R_{14} (cm^{-1})
Ga^{69}	10.23	0.2318	3.5 ± 0.6	1.05×10^{10}
Ga^{71}	12.99	0.1416	1.9 ± 0.2	$0.9\ \times10^{10}$
As^{75}	7.29	0.3	6.5 ± 1.5	1.55×10^{10}

at the International Conference on Magnetic and Electric Resonance and Relaxation. A report in the proceedings[3] of this conference also reviews many other aspects of the linear electric field effects in magnetic resonance.

II. EXPERIMENTAL DETERMINATION OF R_{14}

Copper-doped high-resistivity GaAs crystals were kindly given to us by C. Hilsum of Baldock, England, and by A. Weisberg, RCA Laboratories, Princeton, New Jersey. The resistivity was about 10^9 Ω cm at 77°K, but two- to three-orders of magnitude smaller at room temperature. A platelet of approximate dimensions $10\times10\times1$ mm was cut with broad faces normal to the [111] direction. A drop of indium was attached ultrasonically to these faces. Copper leads were soldered to the indium and the whole face of the crystal was covered with an evaporated silver layer. The contacts held at 77°K. A field strength of 20 000 V/cm could be maintained without undue heating of the crystal, if it were immersed in liquid nitrogen. The voltage was supplied by a battery of 30 dry cells of 300 V each. The crystal-electrode assembly was wrapped by Teflon sheet. A coil of copper wire was wound around it and cemented with Flexrock 80 glue.

The coil was part of the tank circuit of a phase-locked oscillating detector, described by Jeener.[4] A block diagram of the electronic apparatus is shown in Fig 1. The nuclear magnetic resonance was observed near 9 Mc/sec for each of the three isotopes. The required magnetic fields can be deduced from the second column in Table I.

Recordings of the absorption derivative of the Ga resonance, with and without an applied electric field, are shown in Fig. 2. If the angle between the magnetic field $\mathbf{H}_0$ and the [111] direction is denoted by ϑ, the splitting between each satellite transition ($m_I=\frac{3}{2}\rightarrow\frac{1}{2}$ or $m_I=-\frac{1}{2}\rightarrow-\frac{3}{2}$) and the central component ($m_I=\frac{1}{2}\rightarrow-\frac{1}{2}$), due to the induced field gradient given by Eq. (3), becomes

$$h\Delta\nu_E=12^{-1/2}(3\cos^2\vartheta-1)eQ(R_{14}+S_{44}d_{14})E_{111}. \quad (4)$$

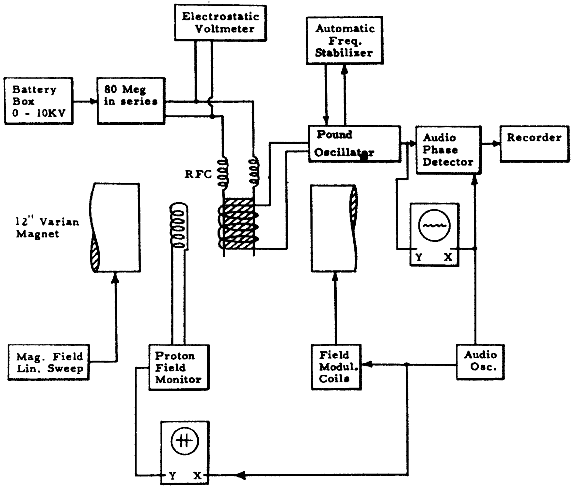

FIG. 1. Schematic block diagram of the experimental equipment to study the electrically induced quadrupole interaction in GaAs.

The experimental values for this splitting at $\vartheta=0$ are listed in the fourth column of Table I. The intensity ratios of the satellites to the central components should be as 3:4:3. The observed satellites appear to be broader and weaker. This is due to a distribution of electric field strength inside the sample. Although fringing fields and nonuniform thickness d of the slab may be partly responsible, the major cause is believed to reside in an inhomogeneous resistivity due to nonuniform doping. This set the limit on the accuracy with which $\Delta\nu_E$ could be determined in the partly resolved multiplets. The contact electrodes and the finite resistivity prevented the formation of double layers and surface charges. The macroscopic field strength inside the sample is immediately given by the applied voltage divided by the thickness.

Independent determinations of S_{44} and d_{14} were carried out. The experiment of Shulman, Wyluda, and Anderson[5] on InSb to determine the quadrupole inter-

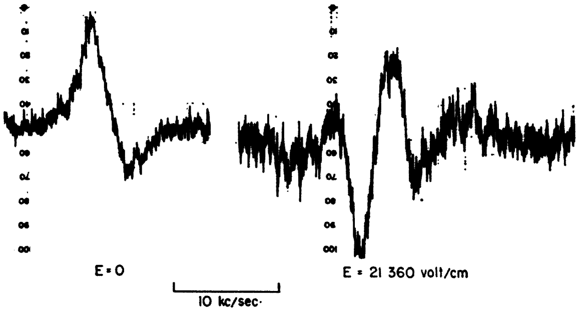

FIG. 2. The splitting of the Ga^{69} nuclear magnetic resonance at 9 Mc/sec in GaAs by an applied electric field of 21.3 kV/cm. Both H_0 and E are along [111]. The derivative of the absorption curve shows incipient saturation. The satellites are broadened by inhomogeneities of the electric field.

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[3] N. Bloembergen, in *Proceedings of the 11th Colloque Ampère, Eindhoven, July 1962* (North-Holland Publishing Company, Amsterdam, 1963), p. 225.

[4] J. Jeener. Rev. Sci. Instr. **32**, 27 (1961).

[5] R. G. Shulman, B. J. Wyluda, and P. W. Anderson, Phys. Rev. **107**, 953 (1957).

action under stress was performed on GaAs samples. A compressive stress T was applied along the [111] direction. For $T=18$ kg/cm^2 no change in line shape was observable for the As^{75} nor for the Ga^{71} resonance. This sets an upper bound on S_{44}. With the known elastic modulus[6] $C_{44}=0.59\times10^{12}$ dyn/cm^2 the electric field gradient induced by the stress T is given by

$$eq^T{}_{111}=\tfrac{2}{3}S_{44}C_{44}{}^{-1}T.$$

Since the magnetic field $\mathbf{H}_0$ was perpendicular to the direction of stress, the stress-induced quadrupole splitting is

$$h\Delta\nu_T=\tfrac{1}{6}C_{44}{}^{-1}S_{44}TeQ. \tag{5}$$

A value $\Delta\nu_T=0.5$ kc/sec would have been observable and, therefore, an upper bound $S_{44}\leq4.5\times10^{15}$ statC/cm^3 could be established.

The piezoelectric constant d_{14} was measured on the same sample by determining the surface charge induced by a compressive stress T on the (111) faces. The polarization along [111] is related to T by

$$P_{[111]}=3^{1/2}d_{14}T_{[1,1,1]}.$$

The induced surface charge was measured by a ballistic galvanometer technique. The transient voltage, developed by application and removal of the stress across a 2500-Ω resistor which shunted the crystal electrodes, was amplified in a Beckman dc Breaker Amplifier, and the oscillographic display recorded by a Land camera. The apparatus was calibrated by repeating the experiment with NaClO$_3$ in the same geometry. The piezoelectric constant of this crystal is known,[7] $d_{14}(\mathrm{NaClO_3})=6.1\times10^{-8}$ cgs units. Reproducible stresses were obtained by hanging a weight on the arm of a drill press. Multiple exposures were taken of the transients, $\int idt$, which are proportional to the weight and the piezoelectric constant, but independent of the dielectric constant and dimensions of the specimen. The result is $d_{14}(\mathrm{GaAs})=(0.32\pm0.08)d_{14}(\mathrm{NaClO_3})$, or $d_{14}(\mathrm{GaAs})=(2.0\pm0.5)\times10^{-8}$ cgs units.

The product $d_{14}S_{44}$ is therefore smaller than 10^8 cgs units. This should be compared with observed values of $R_{14}+d_{14}S_{44}\sim10^{10}$ cm^{-1} which are listed in the last column of Table I. The piezoelectric strain produces less than one percent of the observed effect. The values in the last column which were derived from the observed shifts with the aid of Eq. (4) may, therefore, be identified with R_{14}.

An independent determination of R_{14} for the three isotopes in GaAs has recently been made by Brun and co-workers.[8] They used the technique of saturation of $\Delta m=+2$ transitions by an applied electric radiofrequency field. The electric field is again applied along [111] and the magnetic field $\mathbf{H}_0$ is applied at right angles, so that $\sin\vartheta=1$. The gradient induced by the electric field has off-diagonal quadrupole matrix elements with $\Delta m_I=2$. The requirements on the resistivity of the sample are not as high in this case and this method could perhaps be used successfully in other III–V compounds. The attainable precision is, however, not as high as with the direct splitting of the resonance by a dc field. The values of R_{14} obtained by Brun agree with our results within the limits of error.

III. ATOMISTIC THEORY OF THE LINEAR ELECTRIC SHIFT

An oversimplified model will be used, which will tie in as directly as possible with two other observables, the dielectric constant at low frequencies, $\epsilon=12.5\pm0.2$, and the optical index of refraction in the infrared below the absorption edge,[9] $n=3.3$.

The induced field gradient at the nucleus is caused partly by a distortion of the valence orbitals and partly by a relative displacement Δr of the lattice of the Ga atomic cores with respect to the As core lattice. The static dielectric constant contains two similar contributions. The ionic polarization is related to the difference $\epsilon-n^2$. If an effective charge e_{eff} of opposite sign is put at the position of the Ga and As lattice sites, this polarization is given by

$$Ne_{\mathrm{eff}}\Delta r=[(\epsilon-n^2)/4\pi]E, \tag{6}$$

where $N=2.2\times10^{22}$ is the number of GaAs molecules per unit volume. This equation differs by a factor $3(n^2+2)^{-1}$ from Eq. (12) of reference 3. This factor corrects for the electronic polarization induced by the ionic displacements. It should be applied to the core polarization of the localized electrons in the Ga and As cores. The largest part of the electronic polarizability comes, however, from the valence orbitals. These orbitals are so extended that it is a better approximation to consider the electronic density uniformly distributed over the unit cell and not concentrated on sites with cubic symmetry. In this approximation the effective electric field acting on the valence orbitals is equal to the microscopic *average* field or to Maxwell's macroscopic electric field. For fixed macroscopic E, the electronic polarization is independent of the ionic displacement. This fact was used by Brodsky and Burstein[10] and leads to the simple expression (6).

The electric field gradient at an atomic site can be calculated from the electrostatic theory, if the atom is displaced by a distance Δr from the center of a tetrahedron towards one of the four corners, at which equal charges are placed. The result is $(40/3)e_{\mathrm{eff}}\Delta ra^{-4}$, where $a=2.44$ Å is the Ga-As distance. If the Sternheimer

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[6] T. B. Bateman, H. J. McSkimin, and J. M. Whelan, J. Appl. Phys. **30**, 544 (1959).

[7] W. P. Mason, *Piezoelectric Crystals* (D. Van Nostrand Company, Inc., Princeton, New Jersey, 1948), p. 195.

[8] E. Brun, R. J. Mahler, H. Mahon, and W. L. Pierce, Phys. Rev. **129**, 1965 (1963).

[9] K. G. Hambleton, C. Hilsum, and B. R. Holeman, Proc. Phys. Soc. (London) **77**, 1147 (1961).

[10] M. H. Brodsky and E. Burstein, Bull. Am. Phys. Soc. **7**, 214 (1962).

antishielding factor $1-\gamma_\infty$ is introduced to take care of the distortion of electron orbitals inside the cores, the electric field gradient at the nucleus due to the atomic displacement effect becomes, with the use of Eq. (6),

$$\langle eq^{\text{ion}}\rangle_{111}=\frac{40}{3}(1-\gamma_\infty)\frac{\epsilon-n^2}{4\pi Na^4}E_{111}. \tag{7}$$

With Eq. (3), the contribution to R_{14} becomes

$$R_{14}{}^{\text{ion}}=3^{-1/2}5(1-\gamma_\infty)(\epsilon-n^2)(\pi Na^4)^{-1}. \tag{8}$$

The Sternheimer factors for Ga and As are not known, but may be estimated by interpolation from calculated values.[11] If $(1-\gamma_\infty)=24$ for Ga and 30 for As are assumed, the values $R_{14}{}^{\text{ion}}(\text{Ga})=0.4\times10^{10}$ cm^{-1} and $R_{14}{}^{\text{ion}}(\text{As})=-0.5\times10^{10}$ cm^{-1} are computed, where E is taken as positive if it points from Ga towards the neighboring As atom.

The distortion of the electron orbitals at fixed nuclear positions may be calculated as a perturbation by the electric field on the valence orbitals of the undistorted crystal. Since an average property of the whole valence band is to be computed, localized molecular orbitals should give a fair representation of the average structure of the valence band.[12] The structure of the covalent crystal suggests that tetrahedral orbitals made up of $4s$ and $4p$ orbitals around the Ga and As atoms and pointing along the crystallographic body diagonals are appropriate zero-order wave functions to estimate the magnitude of the effect. Higher excited states, $4d$, $5s$, etc. will be ignored. The four tetrahedral orbitals are treated independently as mutually orthogonal wave functions. The overlap between Ga and As atomic orbitals will be assumed small compared to unity. The representative wave function of the bonding orbital along [111] is under these assumptions

$$\begin{aligned}\psi_{\text{val}}&=(\lambda\psi_{\text{Ga}}{}^{\text{tet}}+\psi_{\text{As}}{}^{\text{tet}})(1+\lambda^2)^{-1/2},\\ \psi^{\text{tet}}&=\tfrac{1}{2}(\psi_{4s}+\psi_{4px}+\psi_{4py}+\psi_{4pz}).\end{aligned} \tag{9a}$$

The corresponding antibonding orbital is characteristic for the wave function in the conduction band

$$\psi_{\text{cond}}=(-\psi_{\text{Ga}}{}^{\text{tet}}+\lambda\psi_{\text{As}}{}^{\text{tet}})(1+\lambda^2)^{-1/2}. \tag{9b}$$

The ionic character of the bond $(1-\lambda^2)(1+\lambda^2)^{-1}$ is about 0.7. The value $\lambda=0.4$ for each of the four bonds corresponds to an effective total charge $e_{\text{eff}}=+2$ on the Ga sites and -2 on the As sites. This figure is in agreement with the modified Szigeti formula,

$$e_{\text{eff}}=\omega_0[M(\epsilon-n^2)/4\pi N]^{1/2}, \tag{10}$$

where $\omega_0=5.04\times10^{13}$ sec^{-1} is the transverse fundamental optical mode frequency, determined by Picus *et al.*[13,14] A factor $3(n^2+2)^{-1}$ has again been dropped[10] in Eq. (10) because of the nearly uniform distribution of charge in the valence orbitals. The ionic character will undergo a fractional change on application of an electric field along the bond direction. This may be described as an admixture of some conduction orbital to the valence orbital wave function. The energy separation $\Delta W=W_v-W_c$ between the bonding and antibonding orbital corresponds to a certain average separation between the valence and conduction bands in the actual crystal. Second-order perturbation theory, bilinear in the quadrupole moment and the applied electric field, gives the change in the energy of the nuclear spin level m_I as

$$2(W_v-W_c)^{-1}(\psi_{\text{val}},m_I|\mathcal{H}_Q|\psi_{\text{cond}},m_I)(\psi_{\text{cond}}|e\mathbf{E}\cdot\mathbf{r}|\psi_{\text{val}}),$$

where $\mathcal{H}_Q$ is given by Eq. (1). Alternatively the change in electric field gradient produced by the field component along [111] may be written as

$$\begin{aligned}\langle eq_E{}^{\text{cov}}\rangle=2eE_{111}(\psi_{\text{val}}|eq|\psi_{\text{cond}})&\\ \times(\psi_{\text{cond}}|r|\psi_{\text{val}})(W_v-W_c)^{-1}.&\end{aligned} \tag{11}$$

With the simplifying assumptions about the wave functions (8) and (9) and the introduction of eq_{at} for the gradient $-\partial^2V/\partial z^2$ produced by an atomic p_z-orbital,[11] Eq. (11) may be rewritten as

$$\begin{aligned}\langle eq_E{}^{\text{cov}}\rangle_{111}=\lambda(1+\lambda^2)^{-1}(W_v-W_c)^{-1}&\\ \times\tfrac{3}{4}eq_{\text{at}}eE_{111}(\psi_{\text{cond}}|r|\psi_{\text{val}}).&\end{aligned} \tag{12}$$

The acting field on the orbital is essentially equal to the macroscopic field parallel to the bond direction. Elementary symmetry considerations show that components perpendicular to the bond direction do not give a linear contribution.

The other orbitals, pointing to the other three corners of the tetrahedron, also produce a field gradient. In the absence of an applied electric field their contribution just cancels the gradient of the first orbital $(\psi_{\text{val}}|eq|\psi_{\text{val}})$. The induced electric field effect of each of these other three orbitals adds, however, one ninth of the expression (12). Label the new bond direction ζ', the first bond direction ζ. The angle between the two body diagonals is $\cos\vartheta_{\zeta\zeta'}=\frac{1}{3}$. Take the coordinate ξ' in the $\zeta\zeta'$ plane, normal to ζ'. The component of the electric field along ζ' is $-\frac{1}{3}E$. The electric field gradient in the primed system has components $eq_{\zeta'\zeta'}$ equal to $-\frac{1}{3}$ times the expression (12) and $eq_{\xi'\xi'}$ equal to $+\frac{1}{6}$ times the same expression. Transforming this field gradient to the unprimed system gives a contribution

$$eq_{\zeta'\zeta'}\cos^2\vartheta_{\zeta\zeta'}+eq_{\xi'\xi'}\sin^2\vartheta_{\zeta\zeta'}=+\tfrac{1}{9}\langle eq_E{}^{\text{cov}}\rangle_{111}$$

The same argument holds for the remaining two orbitals.

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[11] See for example, T. P. Das, and E. L. Hahn, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1958), Suppl. I.

[12] G. Leman and J. Friedel, J. Appl. Phys. 33S, 281 (1962).

[13] G. S. Picus, E. Burstein, B. W. Henvis, and M. Hass, J. Phys. Chem. Solids **8**, 282 (1959).

[14] M. Hass and B. W. Henvis, J. Phys. Chem. Solids **23**, 1099 (1962).

The total field gradient $\partial^2V/\partial\zeta^2$ along [111] is, therefore, obtained by multiplying Eq. (12) by $\frac{4}{3}$. With Eq. (3) this leads to a covalent contribution to R_{14},

$$R_{14}{}^{\rm cov}=\pm\tfrac{1}{2}\times3^{1/2}\lambda(1+\lambda^2)^{-1}(W_c-W_v)^{-1}eq_{\rm at}\times(\psi_{\rm cond}|er|\psi_{\rm val}).\quad(13)$$

The sign of this covalent contribution is the same as the sign for the ionic contribution of each isotope, given by Eq. (8).

Although the dipole moment matrix element could be evaluated directly for the assumed orbitals, it seems more appropriate to derive its value from the observed optical index of refraction. The polarizability of a single covalent along the bond direction is determined by

$$\tfrac{1}{2}\alpha E_{111}{}^2|(\psi_{\rm cond}|er|\psi_{\rm val})|^2(W_c-W_v)^{-1}.$$

The acting electric field is again taken equal to the macroscopic field component along the bond direction. If the induced dipole moments in all four bonds are added vectorially, the total induced electronic polarization is found to be

$$P^{\rm el}=(n^2-1)(4\pi)^{-1}E=(8/3)N\times|(\psi_{\rm cond}|er|\psi_{\rm val})|^2(W_c-W_v)^{-1}E.\quad(14)$$

With $n=3.3$ and $W_c-W_v=2$ eV (the energy gap between the bands is 1.5 eV) a reasonable value of the dipole moment matrix element, $(1.3\times10^{-8}$ cm$)e$, is obtained. If this value is substituted into Eq. (13) with[11] $q_{\rm at}({\rm Ga})+-18.9\times10^{24}$ cm^{-3} and $q_{\rm at}({\rm As})=-40.8\times10^{24}$ cm^{-3} and $\lambda=0.4$, one finds for the covalent contributions $R_{14}{}^{\rm cov}({\rm Ga})=0.53\times10^{+10}$ cm^{-1}, and $R_{14}{}^{\rm cov}({\rm As})=-1.1\times10^{+10}$ cm^{-1}. These results are only slightly larger than the corresponding contributions from ionic displacements. Addition of the two results gives a theoretical value $R_{14}({\rm Ga})=0.93\times10^{10}$ cm^{-1} which coincides fortuitously with the observed values in Table I. The computed value of $R_{14}({\rm As})$ is 1.6×10^{10} cm^{-1} or 10% higher than the observed value.

The oversimplification of the theoretical model clearly does not permit a more detailed discussion. The agreement between theory and experiment is much better than could be expected in view of the drastic approximations in the theoretical model. In particular, the uncertainty in the Sternheimer factors, admixture of other wave functions in the band structure, effective energy separation of the bands, overlap of atomic wave functions, and other contributions to the quadrupole coupling in the covalent orbitals should be calculated more carefully. The basic physical origin of the electric shift of the nuclear quadrupole coupling is, however, well established by this example.

If the less appropriate Lorentz local fields had been used for valence electrons, the value $R_{14}{}^{\rm ion}$ would have been smaller by a factor $3/(n^2+2)\approx\frac{1}{4}$ and $R_{14}{}^{\rm cov}$ would have been smaller by $[3/(n^2+2)]^{1/2}\approx\frac{1}{2}$. The agreement with experiment would be worse.

IV. CONCLUSION

The electric shift in nuclear magnetic resonance provides additional constants, which supplement the information obtainable from dielectric constants, optical index of refraction, etc. The constants are particularly sensitive to the degree of hybridization of wave functions of opposite parity. More detailed theoretical models must be able to account for the additional experimental parameters, provided by the linear electric field effect.

ACKNOWLEDGMENTS

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APPENDIX

Consider an ensemble of nuclear spins quantized along the [111] direction in GaAs by an external magnetic field. If an electric field E is also applied along this direction, the free energy of the system changes according to Eqs. (1) and (3) by,

$$F_{QE}=12^{-1/2}\textstyle\sum_{\rm isotopes}(n_{3/2}+n_{-3/2}-n_{1/2}-n_{1/2})R_{14}eQE.\quad({\rm A1})$$

An electric polarization proportional to the nuclear quadrupole moments can be defined by

$$P_Q=-\partial F_{QE}/\partial E.\quad({\rm A2})$$

If the populations in the nuclear spin states, n_m, are changed, a change in polarization is induced according to Eqs. (A1) and (A2). This effect is the thermodynamic inverse of the experiment described in this paper.

If the nuclear spin system is heated up, e.g., by saturation of a nuclear magnetic resonance, a surface charge is induced on the electrodes at the (111) faces of the crystal. Since for equidistant Zeeman levels

$$n_{3/2}+n_{-3/2}-n_{1/2}-n_{1/2}=\tfrac{1}{2}N(g\beta H_0/kT)^2,$$

where N is the total number of spins, the effect is very small. If, however, a dc electric field is applied and only one electric satellite resonance e.g., $m=\frac{3}{2}\rightarrow\frac{1}{2}$ is saturated, the effect will be linear in $g\beta H_0/kT$. This will also be the case in crystals with zero-field quadrupole splittings. In such situations a change in the nuclear spin populations may be induced, so that

$$\Delta n=\Delta(n_{3/2}+n_{-3/2}-n_{+1/2}-n_{-1/2})\approx\tfrac{1}{2}N(h\nu_0/kT).\quad({\rm A3})$$

If $\nu_0=10^7$ cps, $T=77$°K, and other numerical values are substituted into Eqs. (A1), (A2), and (A3), one finds that the induced polarization is equivalent to a potential drop of 0.4 mV/cm across the GaAs crystal.

For a pure quadrupole resonance of Br or I isotopes, carried out in other piezoelectric crystals at $3–5\times10^8$ cps at 4°K, the effect should be 2 or 3 orders of magnitude larger and should be readily observable. It is necessary that the crystal lacks a center of inversion symmetry. Otherwise the contributions of lattice sites related to each other by the inversion will cancel each other in the summation of Eq. (A1), because they have opposite sign of the tensor elements R.

The physical origin of this "quadrupole-electric effect" is, of course, based on the observation that the equilibrium position of the nucleus in the lattice depends on the orientation of the nuclear quadrupole moment. If the nucleus is at a site which lacks inversion symmetry and has nonvanishing third derivatives of the electrostatic potential, the force on the nucleus is

$$-Ze\nabla V-e\mathbf{rr}:\nabla\nabla\nabla V.$$

The electric field $-\nabla V$ acting on the nucleus is not exactly zero on the average. The equilibrium position of the Ga and As nuclei is not exactly at the center of the tetrahedra, but slightly displaced towards or away from one of the corners, depending on whether the nuclear quantum state has $|m_I|=\frac{3}{2}$ or $\frac{1}{2}$.

The magnitude of the displacement depends on the extent to which the electron orbitals follow the nuclear displacement. The polarization resulting from all nuclear and electronic displacements is, however, unambiguously determined by Eqs. (A1) and (A2). If the model from Sec. III of ionic displacements with an effective charge is adopted, the spatial displacement δr of a nuclear spin, while making a $|m_I|=\frac{3}{2}\rightarrow\frac{1}{2}$ transition, is given by

$$e_{\mathrm{eff}}\delta r=2^{-1/2}R_{14}{}^{\mathrm{ion}}eQ. \qquad \text{(A4)}$$

This displacement is about 2.5×10^{-16} cm, much smaller than the zero-point vibration of an individual nucleus or even the nuclear dimension. The combined effect of all spin transitions in the ensemble of nuclear spins in the crystal leads, however, to a macroscopically observable polarization. The difference in equilibrium position of a nuclear spin in the $|m_I|=\frac{3}{2}$ or the $|m_I|=\frac{1}{2}$ is an example of a Jahn-Teller distortion to lift the fourfold degeneracy of the nuclear spin levels into two Kramers doublets. The effect is so small that, in the absence of external fields, each nucleus would "tunnel" rapidly between the four equivalent positions along the four body diagonals.

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Electron Ejection from Metals due to 1- to 10-keV Noble Gas Ion Bombardment. I. Polycrystalline Materials*

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A method is described which complements present techniques and enables measurements to be made of the secondary electron emission coefficient, γ, for ions on materials for which γ is difficult or impossible to measure by the "flashing" or heating technique. The method allows operation in a high-vacuum (10^{-8} Torr) system as opposed to an ultra-high vacuum ($<10^{-9}$ Torr) system. Results for the secondary electron emission coefficient, γ, are presented for Ar^+ on Zr, Cu, Mo, Ni, Ta, and Al, and for Ne^+, Kr^+, and Xe^+ on Cu and Mo in the energy range 0.5 to 10.0 keV. Comparisons with present theories and with other experimental results are made.

I. INTRODUCTION

INTEREST in the study of the secondary electron ejection from atomically clean surfaces due to positive ion bombardment has been stimulated, at least in part, by the advanced vacuum techniques now available. For example, many of the data obtained by earlier investigators are open to question because of surface contamination,[1] due in part to poor vacuum conditions. During the past decade, Hagstrum has published a great deal of significant research on the measurement of γ, the secondary electron emission coefficient, from various refractory metals[2] and semiconductors[3] subjected to noble gas ion bombardment. Hagstrum's work was done in the energy range from 10 to 1000 eV. In this energy range electron emission occurs by the potential ejection mechanism which is a result of Auger neutralization and de-excitation.[4] Hagstrum has also demonstrated the strong influence of

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[1] For a good review of the subject prior to 1956 see H. S. W. Massey and E. H. S. Burhop in, *Electronic and Ionic Impact Phenomena* (Oxford University Press, New York, 1952), Chap. IX.

[2] H. D. Hagstrum, Phys. Rev. **89**, 244 (1953); **96**, 325 (1954); **104**, 672 (1956); **104**, 317 (1956).

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[4] H. D. Hagstrum, Phys. Rev. **96**, 336 (1954).