Knight Shifts and Linewidths of the Pb^{207} Nuclear Magnetic Resonance in Lead-Indium Alloys*

REX J. SNODGRASS† AND LAWRENCE H. BENNETT
National Bureau of Standards, Washington, D. C.
and
The University of Maryland, College Park, Maryland
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The nuclear magnetic resonance of Pb^{207} was observed and accurately measured at room temperature and 77°K, in pure lead metal powder and in a series of lead-indium alloy powders containing up to 75% indium. Upon the addition of indium, the central frequency of the Pb^{207} absorption line increases by a small fraction of the linewidth. At 5 Mc/sec, this frequency shift between pure lead and 20 at. % In is 800 cps, compared to a linewidth of 14 kc/sec in the 20 at. % In sample. The increase in frequency is also a small fraction of the Knight shift, $\Delta k/k=1.1\%$ up to 20 at. % In. In the cubic lead phase, the frequency shift is linear with composition. Volume effects which may be of sufficient magnitude to cause appreciable frequency shifts preclude the possibility of a definite conclusion regarding charge oscillations of the type discussed by Friedel and others. From the temperature dependence of the linewidth, the spin-lattice relaxation time is found to be $T_1=3.6\times10^{-4}$ sec at 77°K. The linear field dependence of the linewidth in the alloys is primarily attributed to anisotropic Knight-shift broadening, although isotropic Knight-shift broadening is not excluded. Upon alloying, the low-field absorption linewidth increases rapidly due to a combination of indirect spin exchange and pseudodipolar coupling, and the line shape changes from Lorentzian toward Gaussian. A second moment analysis yields a value for the near-neighbor exchange constant $h^{-1}|A_{Pb-In}|=0.9$ kc/sec. The pseudodipolar exchange constant is found to be $h^{-1}|B_{Pb-In}|=1.0$ kc/sec. Large values for the ratio B_{Pb-In}/A_{Pb-In} and the ratio of pseudodipolar to classical dipolar indicate that the amount of p character probably greatly exceeds the amount of s character in the electron wave functions at the Fermi surface in this alloy and is consistent with the observation of anisotropic Knight-shift broadening.

I. INTRODUCTION

THIS paper describes the results of an investigation of the nuclear magnetic resonance of Pb^{207} in pure lead and in a series of lead-indium alloys.[1] The purpose of this study is to achieve a better understanding of the changes in nuclear and electronic properties of a multivalent host lattice when impurities are added. It is desirable to determine the perturbation on the charge density at the host atoms caused by the addition of impurities. In particular, it is of interest to see if the long-range oscillations of electronic charge density around an impurity atom which have been successful in explaining the large Knight-shift variations and rapidly increasing widths in "simple" (mono- or divalent) metals such as silver,[2,3] cadmium,[3] and the alkali metals[4] also are important for polyvalent metals which have a complex band structure.

Lead, a column IV element, was chosen for study because it has no nuclear electric quadrupole moment and because it forms a solid solution over a considerable range with elements around it in the Periodic Table. Pb^{207} has a nuclear spin $I=\frac{1}{2}$, a natural abundance of 21%, and is the only magnetic isotope. Indium is the solute in this investigation. Indium, a column III element, has two stable isotopes, each with nuclear spin $I=\frac{9}{2}$, and each possessing large magnetic dipole and electric quadrupole moments. In^{115} is 96% abundant, In^{113} is 4% abundant. Most measurements were taken in the fcc Pb phase of the alloy which extends to about 68 at. % In. The phase diagram[5] is shown in Fig. 1.

Nuclear magnetic resonance (NMR) central frequencies, absorption linewidths, and line shapes of the Pb^{207} nuclei are analyzed. The experimental data are discussed in terms of changes in electronic band structure, perturbation of the effective magnetic field at the

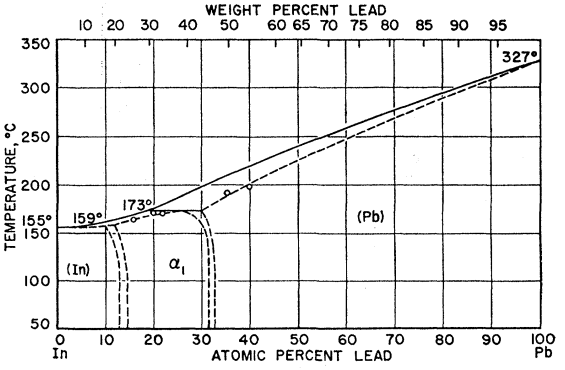

FIG. 1. Pb-In phase diagram (after Hansen, Ref. 5).

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† Guest worker (1963–64), University of Paris, Faculté des Sciences-Orsay (Group II), Service de Physique des Solides, Orsay (S.-et-O.), France.

[1] A preliminary report of part of this work was given by R. J. Snodgrass and L. H. Bennett, Bull. Am. Phys. Soc. 7, 227 (1962).

[2] T. J. Rowland, Phys. Rev. 125, 459 (1962).

[3] L. E. Drain, Phil. Mag. 4, 484 (1959).

[4] L. Rimai and N. Bloembergen, J. Phys. Chem. Solids 13, 257 (1960).

[5] M. Hansen, *Constitution of Binary Alloys* (McGraw-Hill Book Company, Inc., New York, 1958), p. 855. Used by permission.

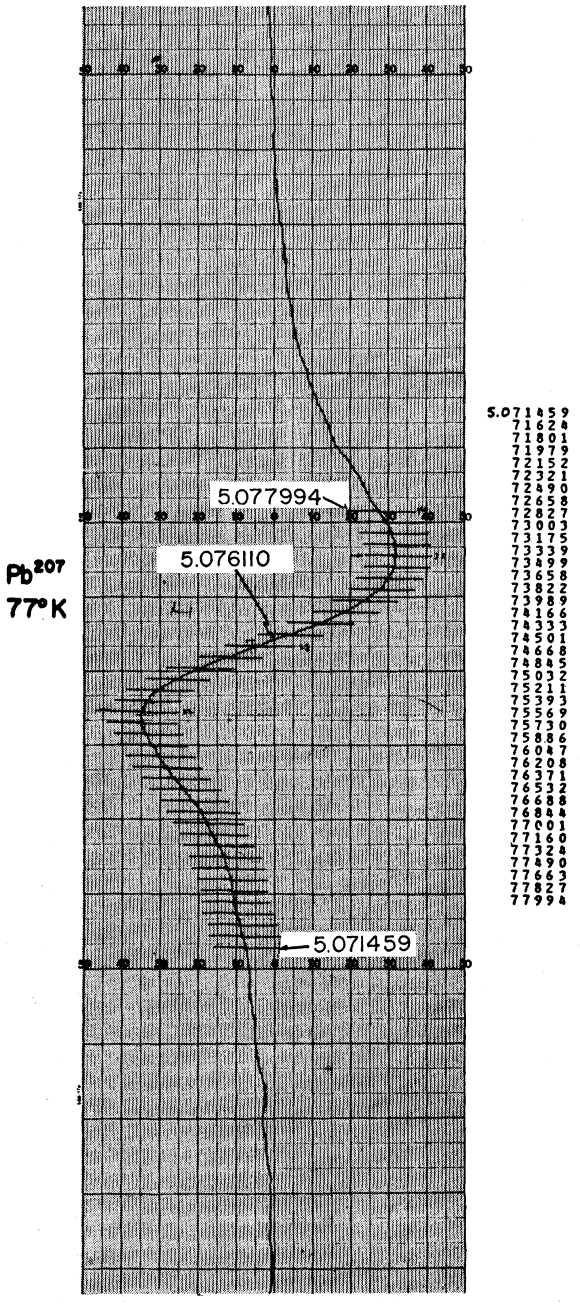

FIG. 2. Nuclear magnetic resonance curve of Pb^{207} at 77°K showing frequency markers about 200 cps apart. Frequency values corresponding to each marker are automatically recorded.

nuclear sites, magnetic interactions, and relaxation mechanisms.

The experimental technique, including a discussion of those factors which affect the accuracy of the measurements, is described in Sec. II. Section III presents the experimental results. The line shape in pure lead metal is Lorentzian. The central frequency of lead increases by a *small fraction of the linewidth* upon addition of indium. The absorption line broadens rapidly with indium concentration, and, for the alloys, with magnetic field. The Knight-shift results are compared with the work of others in Sec. IV A. Unfortunately, the unknown volume dependence precludes the possibility of a definite conclusion concerning the importance of charge oscillations in the Pb-In system. On the free electron model the volume dependence of the Knight shift rests on a precarious balance of terms, each of which is comparable in magnitude to the observed Knight shift. In Sec. IVB., the contributions of the different line broadening mechanisms are listed. The spin-lattice relaxation time in lead metal is obtained from the temperature dependence of the linewidth. The field-dependent part in the alloys is attributed to anisotropic Knight-shift broadening, although the inhomogeneous isotropic Knight shift cannot be ruled out. The increase in linewidth at low fields, with increasing concentration, is attributed to a combination of indirect exchange and pseudodipolar coupling. From the data, we deduce values for the exchange constants A and B. The paper is summarized in Sec. V.

II. EXPERIMENTAL METHOD

A Varian wide-line nuclear induction spectrometer was used for all of the measurements. Maximum rf transmitter power, corresponding to H_1 equal to about 1 G, was used to obtain the best signal-to-noise ratio for lead samples containing more than about 10 at. % indium. For the low indium concentration samples at 77°K, the rf level H_1, was reduced to about $\frac{1}{2}$ G in order to minimize possible saturation effects. The method for making measurements on metal powders at 77°K using the Varian spectrometer has been discussed elsewhere.[6] Audio modulation of 80 cps was used for most curves. Modulation frequencies as high as 400 cps caused no observable effect on the resonance line due to the large linewidth and short spin-lattice relaxation time T_1, estimated in Sec. IV to be about 10^{-4} sec. The time taken to sweep through a resonance varied from about 30 sec for pure Pb to 10 min for the 80%-In sample. The time constant of the output circuit following the phase-sensitive detector was 25 sec for the broader curves, and 3 to 10 sec for the narrower ones, thereby avoiding distortion of the line. The usual procedure, when using this commercial spectrometer, is to sweep the magnetic field through resonance, holding the spectrometer frequency constant. However, in these experiments, in order to obtain greater measurement accuracy, the frequency of the spectrometer was varied and the steady field held constant. A Varian F-8 NMR fluxmeter utilizing a proton sample about 0.2 Oe in width was used to control and measure the field. The field was held constant to within about ± 0.05 Oe, corresponding to about ± 50 Pb^{207} cycles at 8 Mc/sec. The difference in field at the sample and fluxmeter

[6] R. J. Snodgrass and L. H. Bennett, Appl. Spectry. 17, 53 (1963).

probe positions, which can easily be as much as 0.2 Oe, was corrected for by simultaneously observing protons in the fluxmeter and Na^{23} in a saturated solution of sodium chloride in the sample position. The correction, which eliminates the uncertainty due to changing the position of either probe, involves holding the ratio $\nu(H^1)/\nu(Na^{23})$ constant for all measurements. All frequencies were measured with a frequency counter whose crystal was calibrated against the NBS standard reference frequency. Voltage pulses from the frequency counter were used to put frequency pips about 200 cps apart on the recorded resonance, the value of frequency being simultaneously printed out. A typical resonance curve is shown in Fig. 2. Using this technique, the central frequency of a broad, weak line can be measured to within about 1% of the linewidth. When the resonance was difficult to observe, or when studying line shapes, the field was swept and frequency held constant.

To determine the "center" of a recorded absorption derivative curve, several common methods were used. When the different methods, applied to the same curve, gave values of the central frequency which differed by more than about a hundred cycles per second, that curve was discarded. Generally, the center was picked by tracing the curve and then rotating the tracing through 180°. Superposition of the two curves locates the center of symmetry. We conclude that the pure lead resonance is symmetric since the variations of individual resonances from perfect symmetry are random. Resonances were repeated from four to ten times or more and the error in obtaining the center estimated from the differences between the individual results.

The measurements were taken on 325-mesh particles. No essential differences were noted in measurements on 99.99% and 99.999% pure lead. Microscopic analysis of particle size distribution showed that the average diameter was about 20 μ. The particles are roughly spherical. To avoid distorting the line shape and shifting the center due to eddy current effects, the ratio $p=2t/\delta$ should be less than 1. Here $2t$ is the particle diameter and δ is the skin depth. The smallest δ occurs at 77°K for pure lead and for indium rich (>75 at. % In) samples. The resistivity ρ is about the same in these samples ($\rho\sim 4\,\mu\Omega$ cm). For this case, at 5 Mc/sec, $\delta=47\,\mu$, and $p=0.43$, for 20 μ material. At 7 Mc/sec, $p=0.50$. The magnitude of the shift of the central frequency due to eddy currents[7] is proportional to the linewidth and for $p=1$ (average particle size equal to skin depth) amounts to about 30 cps for pure Pb at 77°K. The largest shift occurs in the large linewidth samples, and for a 20-kc/sec linewidth, is about 300 cps. The shift is to a lower frequency. No correction has been applied to the data for this effect. The amount of eddy-current effect contained in the experimental value of the frequency depends on the method for picking the center. The eddy-current shifts given above

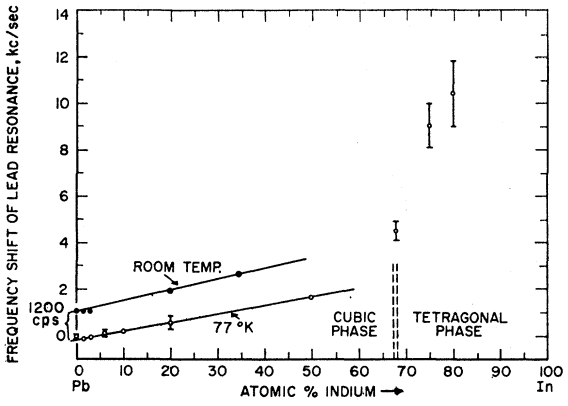

FIG. 3. Change in Knight shift at 5.6 kOe of Pb^{207} versus In concentration at 77 and 300°K.

are those that will be realized if the central resonance frequency is picked by using the off-resonance baseline. Any other method of picking the center, for example, 180° superposition, compensates for a considerable part (over half) of the shift.

III. EXPERIMENTAL RESULTS

A. Knight Shift

Experimentally, the Knight shift is obtained by measuring the resonance frequencies ν_m and ν_r of a metallic sample and a nonmetallic salt, respectively, the external field being the same for both measurements. The Knight shift is given by $k=(\nu_m-\nu_r)/\nu_r$. Differences in chemical shifts of the salt compounds can easily cause k to vary by 20%. We take[8,9] $k=1.47\%$ corresponding to the reference frequency ν_r of $PbSO_4$. However, the values for the change in Knight shift $\Delta k/k$ given below do not sensitively depend on this choice of k. The ratio of the measured resonance frequency and field for lead metal at 77°K is $\nu^{207}/H^{207}=0.90047\pm0.00002$ kc/(sec·Oe). For this measurement it is assumed that the ratio $\nu^1/\nu^{23}=3.780500$ when the fields are the same for both isotopes.

The change in Knight shift Δk of the Pb^{207} nuclei as a function of indium concentration at 77°K and room temperature is shown in Fig. 3. The frequency shifts are plotted relative to the central resonance frequency of pure lead at 77°K. The error bars represent two-thirds of the standard deviations of several experiments. The most important feature of these curves is that the shifts are *small*. At 5 Mc/sec, the increase in resonance frequency in going from pure lead to 20 at. % indium is only 800 cps which gives $\Delta k/k=1.1\%$. These 800 cps represent only 6% of the linewidth of the 20% sample at 77°K. This result is in contrast to the large shifts observed by Rowland,[2] Drain,[3] and Bloembergen and Rimai[4] in mono- or divalent metals. Our results are compared with other work in Sec. IV.

[7] A. C. Chapman, P. Rhodes, and E. F. W. Seymour, Proc. Phys. Soc. (London) **70B**, 345 (1957).

[8] L. H. Piette and H. E. Weaver, J. Chem. Phys. **28**, 735 (1958).

[9] T. J. Rowland, Prog. Mater. Sci. **9**, No. 1 (1961).

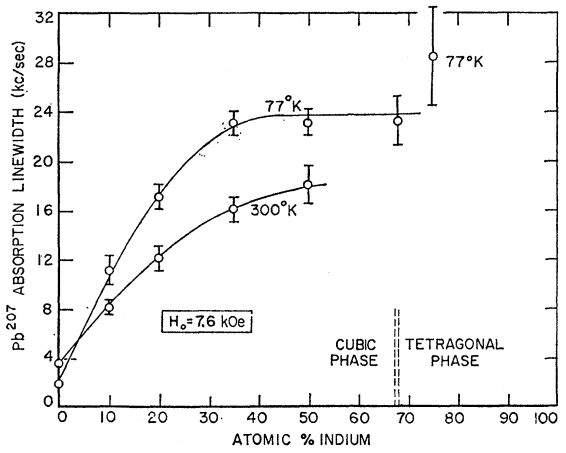

FIG. 4. Linewidth of Pb^{207} at 7.6 kOe versus In concentration at 77 and 300°K.

The Pb^{207} frequency shift versus indium concentration is linear, within experimental error, out to 50 at. % In, as shown in Fig. 3. The two highest In-concentra- points, obtained at 77°K, fall in the α_1-tetragonal lattice. The electronic structure and atomic volume in this phase differ from that of the cubic phase. For this reason, these two points are not expected to join smoothly with the cubic phase points. The 68% sample was made with the objective of obtaining a sample with two phases present. It was initially hoped that the shift between the two lines in the two-phase region would be large enough to enable them to be separately observable. However, due to the combination of small shifts and large linewidths only a single line was observed. The frequency shift of this line shows that it is most likely composed of two lines, separated by about one-third of the linewidth, characteristic of the two phases present at this concentration of indium. However, x-ray analysis showed the 68% point to lie mostly in the cubic phase. If the resonance in this sample is characteristic of the cubic phase only, then we may be observing phase boundary effects. It would be necessary to measure other samples with slightly lower In concentrations to test this interesting possibility.

Figure 3 shows that the frequency versus composition lines at 77°K and at room temperature are parallel to within 150 cps, indicating that the mechanism producing the shift as a function of concentration is largely independent of temperature. In addition, this parallelism implies that the shift as a function of temperature is independent of concentration. Any explanation of the temperature dependence of the resonance position, e.g., in terms of electron-lattice interaction,[10] must be consistent with this fact. The displacement of 1200 cps between the two lines is in close agreement with Feldman's result[10] for pure lead.

[10] D. W. Feldman, Ph.D. thesis, University of California, 1959 (unpublished).

B. Linewidth and Shape

Figure 4 shows the peak-to-peak absorption derivative linewidth of Pb^{207} at 7.6 kOe as a function of indium concentration at 77°K and room temperature. The line broadens rapidly as indium is added, at both temperatures. At 77°K, the linewidth increases from 2 kc/sec[11] in pure Pb to about 24 kc/sec in the high In-concentration samples. In Sec. IV B we attribute the crossing of the two lines in Fig. 4 to the temperature dependence of the spin-lattice relaxation.

The linewidth in the alloys depends linearly on the externally applied magnetic field at both temperatures, as shown in Fig. 5 for the 80% Pb-20% In alloy. At the field strength (7.6 kOe) of Fig. 4, the field-dependent contribution already accounts for more than half the width of the 20% In sample. The linewidths as a function of In concentration at values of applied field from 4.5 to 12.3 kOe are shown in Fig. 6. Also shown is the zero-field linewidth, obtained by extrapolating the width versus field curve for each sample to zero field.

In order to determine any change in line shape, two methods were used. In the first, the resonance lines were normalized and superposed on the ideal Lorentzian and Gaussian shapes. In the second, the ratio of the peaks of the dispersion derivative was measured. The line shape of Pb^{207} in pure lead is Lorentzian at both temperatures. As indium is added to lead, the shape of the Pb line changes qualitatively, at constant field, from Lorentzian to a mixture of Lorentzian and Gaussian. At 10% In, the shape still fits the Lorentzian, but by 35% In the line is a mixture of the two ideal shapes, fitting the Gaussian somewhat better. The ratio of the dispersion peaks in the 10%-In sample remained approximately 8:1, the ideal Lorentzian value, at 12 kOe. The change in line shape from Lorentzian toward Gaussian, as the abundance of the unlike species is increased, had been observed previously in the isotopes

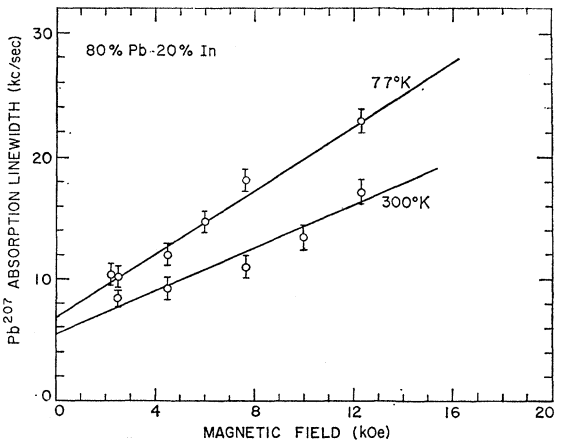

FIG. 5. Pb^{207} absorption width versus applied field in Pb^{207}—20% In at 77 and 300°K.

[11] N. Bloembergen and T. J. Rowland, Acta Met. 1, 731 (1953).

of thallium.[12] An indirect exchange interaction[12,13] $AI_1 \cdot I_2$ between a pair of unlike nuclear spins was thought to be responsible for the Gaussian shape and large width in thallium and other heavy isotopes. In the next section, a similar interpretation is given for the change in shape and zero-field width of the Pb^{207} line upon addition of indium.

A value for the experimental root-mean-square second moment, $\Delta\nu$, was obtained from the pure lead resonance line. This value equals approximately the observed peak-to-peak linewidth $\delta\nu$ if, in the second moment determination, the experimental line is truncated at approximately the point where the signal and noise become equal. In our analysis we therefore use $\delta\nu=\Delta\nu$ when the line is Lorentzian. A different criterion[12] which is sometimes used is to take the half-width at half-intensity as representing the second moment for a Lorentzian line. This differs by only 15% from our condition and would not appreciably alter any results. For Gaussian lines we use the usual relation $\delta\nu=2\Delta\nu$. For the latter, truncation is not necessary since the wings of the line converge rapidly.

IV. COMPARISON OF THEORY AND EXPERIMENT

A. Shift

Friedel and co-workers,[14–16] have given general formulas for the long-range oscillations of electronic charge density believed to exist around solute atoms in metals. These oscillations seem to be important in explaining the widths and large changes in Knight shifts in mono and divalent metals.[2–4] In these cases, values of $\Delta k/k$ from $0.3c$ to $0.6c$ were observed, where

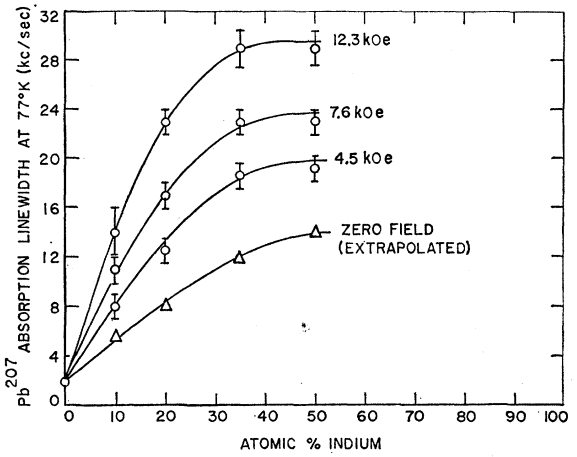

FIG. 6. Pb^{207} absorption width versus indium concentration at different values of applied field.

c is the solute concentration. The theoretical values for these Knight shift changes are in good agreement with these experimental results. However, accurate quantitative calculations of these oscillations are not possible as the exact phase shifts which describe the scattering process in this theory are unknown. The simplifying assumptions involved become more questionable for multivalent materials.

The shifts reported in this paper for the Pb-In system, $\Delta k/k=0.055c$, are almost an order of magnitude smaller than the values for the mono and divalent metals. We have not, however, attempted to calculate the effects of the oscillations of the charge density for Pb-In. The small shifts of the Pb^{207} are perhaps to be compared with the work of Webb[17] on Al^{27} doped with Zn or Mg. For either solute, the shift of the Al^{27} center was too small to be detected, with the conclusion that $|\Delta k/k|<0.1c$. Using the results of Blandin and Friedel,[18] Webb computed the change in the average solvent Knight shift which would be produced by the oscillating charge distribution around the solute atoms and found $\Delta k/k=-0.29c$ for AlZn, and $-0.43c$ for AlMg. Shifts as large as these would have been detected. Webb concluded that the shifts predicted by the charge oscillation theory are not in quantitative agreement with his experiment.

We show below that volume effects may not be neglected in our case. For silver alloys, volume effects were an order of magnitude too small to explain the shifts and were properly ignored. In our case, and for Webb's experiments, they may be large, being perhaps comparable to the observed shift itself. The volume dependence of the Pauli susceptibility and the wave function at a nucleus are not known with great accuracy for a real metal or alloy. For this reason, a prediction even of the direction of the frequency change accompanying alloying is difficult. The frequency may increase or decrease, depending on the relative importance of the different factors.

For cubic symmetry the Knight shift may be written[19,20] $k=(8\pi/3)\chi_p P_f$, where χ_p is the average electron spin susceptibility per atom, and $P_f=\langle|\psi(0)|^2\rangle$ is the probability density at the nucleus averaged over electrons having energies near the Fermi limit. We seek to explain variations in the shift by variations in the two factors, χ_p and P_f. Thus,

$$\Delta k/k=\Delta\chi_p/\chi_p+\Delta P_f/P_f. \quad (1)$$

For a qualitative understanding of the physical process involved, we assume a free-electron model and consider first the change of Knight shift with temperature. The temperature dependence of the shift may be

[12] N. Bloembergen and T. J. Rowland, Phys. Rev. **97**, 1679 (1955).
[13] M. A. Ruderman and C. Kittel, Phys. Rev. **96**, 99 (1954).
[14] J. Friedel, Phil. Mag. **43**, 153 (1952).
[15] A. Blandin, E. Daniel, and J. Friedel, Phil. Mag. **4**, 180 (1959).
[16] A. Blandin, E. Daniel, J. Phys. Chem. Solids **10**, 126 (1959).
[17] M. B. Webb, J. Phys. Chem. Solids **20**, 127 (1961).
[18] A. Blandin and J. Friedel, J. Phys. Radium **21**, 689 (1960).
[19] C. H. Townes, C. Herring, and W. D. Knight, Phys. Rev. **77**, 852 (1950).
[20] W. D. Knight, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1956), p. 93.

explained[21] in first approximation by the volume change which accompanies thermal expansion at constant pressure. In this approximation, both χ_p and P_f are independent of temperature at constant volume. As the volume increases, the density of states increases, causing a corresponding increase in the susceptibility. For n free electrons per atom, $\chi_p \propto V^{2/3}n^{1/3}$, where V is the atomic volume. Assuming that the number of electrons does not change with temperature the fractional change in χ_p is $\Delta\chi_p/\chi_p = 2\Delta V/3V$. For lead, $\Delta V/V = +1.8\%$ for a temperature change from 77 to 300°K. Thus $\Delta\chi_p/\chi_p = +1.2\%$ due to thermal expansion. In the free-electron picture, $P_f \propto V^{-1}$, from normalization, and $\Delta P_f/P_f = -\Delta V/V = -1.8\%$. Hence, the shift predicted by this model is $\Delta k/k = -0.6\%$, compared to the measured shift $\Delta k/k = +1.6\%$.

Although even the direction of the predicted shift is incorrect on this simple model, the magnitudes of the separate terms involving χ_p and P_f due to volume changes are comparable to the observed shift due to temperature changes. Since this is the case it seems reasonable to apply this simple theory to determine the importance to the change in Knight shift of the volume changes which accompany alloying.

Mechanisms which can cause a change in the Knight shift at constant volume have been considered in some detail,[22,23] and can produce a positive shift in P_f of the right magnitude. The pressure dependence of the lead Knight shift, which enables one to separate the temperature dependence of $\chi_p P_f$ at constant pressure and at constant volume, has not been measured.

The addition of indium to lead may affect the Knight shift through changes in the volume of the unit cell and changes in the electronic structure of the conduction band. This separation into "volume effects" and "valence effects" is somewhat artificial since ultimately it is the interaction of the electrons (core and conduction) which determines the low-energy positions of the atoms, and consequently the volume per atom. Nevertheless, one can gain some insight into the process of alloying by making this distinction.

Consider the effect of alloying on χ_p.[9] Assuming a free-electron dependence as before, $\chi_p \propto a^2 n^{1/3} = a^2(p+cZ)^{1/3}$, for nondilute solutions, where p and $p+Z$ represent the number of valence electrons per atom of the solvent and solute, respectively, and a is the alloy lattice parameter. Thus,

$$\Delta\chi_p/\chi_p = 2\Delta a/a + Z\Delta c/3(p+cZ). \quad (2)$$

When indium is added to lead, the lattice parameter of the cubic lead lattice decreases. The first, or volume, term of Eq. (2) is, therefore, negative. Indium is deficient by one valence electron compared to lead, if one simply compares the free atoms and, consequently, without considering charge oscillations, might be expected to *reduce* the number of electrons in the Pb conduction band and, hence, to reduce the hf interaction producing the Knight shift. The second, or "electron per atom" term, is therefore also negative. Considering only the volume term, in going from pure lead to 80% Pb-20% In, $(\Delta\chi_p/\chi_p)_{\text{Volume}} = -1.5\%$. A better value of χ_p could be obtained from electronic specific heat measurements in the alloys. The valence term is $(\Delta\chi_p/\chi_p)_{\text{Valence}} = -1.8\%$.

The change in the wave function on this model is $\Delta P_f/P_f = -\Delta V/V = +2.2\%$. It should be remarked that the volume change due to alloying is essentially different than that due simply to thermal expansion. For dilute alloys, the atomic volumes vary from atom to atom. Nonetheless, for this calculation we use the usual relationship $\Delta V/V = 3\Delta a/a$. The predicted change in Knight shift from volume effects alone is thus $\Delta k/k = +0.7\%$. Experimentally, $\Delta k/k = +1.1\%$ over this concentration range. As in the analysis of thermal expansion, the magnitudes of the separate terms are comparable to the observed shift. Inclusion of the second, or valence term, in Eq. (2), would predict a negative shift. It is clear that the measured Knight shift cannot be explained by the simple notion of the transfer of charge from the Pb to In atoms with subsequent Thomas-Fermi screening, since this produces a shift in the opposite direction to that observed. The inadequacy of the Thomas-Fermi model has been previously established.[2-4]

In conclusion, the absence of accurate knowledge of the change in Knight shift due to volume changes precludes the possibility of confirming or denying the existence of charge oscillations in the lead-indium system. It is hoped that experiments on other lead alloys will facilitate the correlation of the observed shift with solute valence and size.

It is possible that there is an additional source of frequency shift contained in the nuclear $I_1 \cdot I_2$ exchange coupling via the hyperfine interaction. This may arise from the longitudinal term in the indirect exchange portion of the interaction Hamiltonian. The transverse terms are responsible for the rapid broadening of the zero-field Pb^{207} line upon the addition of indium, as is discussed fully in the next section. The exchange broadening in the Pb-In system is large compared with the observed frequency shifts, in contrast to the Ag, Cd, and the alkali alloy systems in which the shifts are larger than the exchange broadening. Thus, although this additional source of frequency shift was not considered in these earlier cases, it may not be negligible in our case, or, in fact, in other heavy element alloy systems.

B. Linewidth

The measured Pb^{207} linewidth may be decomposed into several separate contributions. The analysis is

[21] B. R. McGarvey and H. S. Gutowsky, J. Chem. Phys. **21**, 2114 (1953).
[22] T. Muto, S. Kobayasi, M. Watanabe, and H. Kozima, J. Phys. Chem. Solids **23**, 1303 (1962).
[23] G. B. Benedek and T. Kushida, J. Phys. Chem. Solids **5**, 241 (1958).

TABLE I. Contributions to the second moment ($\Delta\nu^2$) of the Pb^{207} absorption linewidth in lead-indium alloys at 77°K. The "corrected linewidth" has been corrected for the T_1 (cf. Table II) and the field-dependent contributions. Exchange narrowing is not included in the Table.

Sample At. %	Corrected linewidth kc/sec	Dipolar and pseudodipolar $\Delta\nu^2$ (kc/sec)^2	Indirect exchange broadening $\Delta\nu^2$	Classical dipolar alone $\Delta\nu^2$
Pure Pb^{207}	1.4	1.96	0	0.02
90 Pb-10 In	5	17	8	0.18
80 Pb-20 In	7.5	34	22	0.36
65 Pb-35 In	11.5	57	···	0.61
50 Pb-50 In	13.5	84	···	0.89

discussed below. Table I lists the approximate contributions of the different line broadening mechanisms as a function of indium concentration at 77°K. The "corrected linewidth" has been corrected for T_1 and field-dependent linewidth broadening as discussed below. The second moment $\Delta\nu^2$ for each separate mechanism is listed. If the resonance line is broadened by two independent Lorentz mechanisms, producing linewidths a and b, the over-all linewidth $c=a+b$. Usually, however, the second moment due to each mechanism is additive, i.e., $c^2=a^2+b^2$, as for a Gaussian. A Gaussian lineshape is separately produced by the classical dipolar, pseudodipolar, and isotropic indirect exchange broadening interactions, while relaxation broadening leads to a Lorentzian line. The line shape for anisotropic Knight-shift broadening has been discussed[11] by Bloembergen and Rowland. Inhomogeneous isotropic Knight-shift broadening produces[16] a Lorentzian line shape at small solute concentrations, and a Gaussian line shape above a few percent solute. The concentration above which the line is Gaussian depends on the range of oscillations. For twelve nearest neighbors only, the curve should be Gaussian above 3%. For longer range oscillations, the percent is lower. Exchange narrowing produces a Lorentzian shape by narrowing the central portion of the resonance line, while not affecting the second moment. It is believed that a combination of exchange narrowing and T_1 broadening is responsible for the observed Lorentzian line in pure lead and the low indium concentrations.

We attribute the increase in linewidth, in pure lead, from 1.9 kc/sec at 77°K to 3.4 kc/sec at room temperature to spin-lattice relaxation time broadening. The measured linewidth, which is characterized by the total spin-spin relaxation time T_2, has a spin-spin (T_2') and a spin-lattice (T_1) contribution. For Lorentzian lines, $1/T_2=1/T_2'+1/T_1$, and the relation between linewidth $\delta\nu$ and relaxation time is $\delta\nu=1/\sqrt{3}\pi T_2$. Assuming the validity of the Korringa[24] relation, $(T_1)_{77}/(T_1)_{300}=(3.9)\times(1.02)^2=4.1$. Using the measured values of the linewidth at 77°K and room temperature, and assuming that T_2' does not change appreciably between these temperatures, we calculate $T_1=3.6\times10^{-4}$ sec at 77°K, and $T_2'=1.3\times10^{-4}$ sec. The linewidth contributions of T_1 and T_2' are shown in Table II. The preceding value of T_1 is in excellent agreement with the value of 3.6×10^{-4} sec calculated directly from the Korringa relation using the observed Knight shift ($k=1.47\%$) and with the value 3.8×10^{-4} sec, obtained by pulse techniques.[25]

TABLE II. Spin-spin (T_2') and spin-lattice (T_1) contributions to pure lead linewidth in kc/sec.

	$\delta\nu$	$\delta\nu$ (T_1)	$\delta\nu$ (T_2')
77°K	1.9	0.5	1.4
300°K	3.4	2.0	1.4

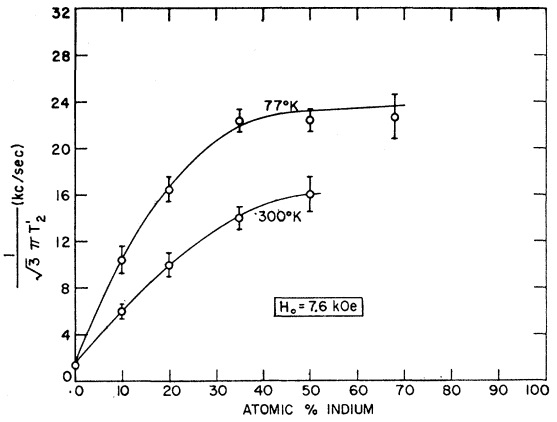

FIG. 7. Corrected linewidth of Pb^{207} versus In concentration at 7.6 kOe. $1/(\sqrt{3}\pi T_2')$ is the Pb^{207} linewidth minus the spin-lattice contribution as discussed in the text.

Figure 4 shows that the width of Pb^{207} at room temperature is greater than that at 77°K for low indium concentrations at a given field. However, at about 4 at. % In and above, the room temperature width falls below that at 77°K. If the temperature-dependent spin-lattice contribution is assumed to be the same in the alloys as in the pure lead and is subtracted out, the crossover is eliminated and the curves appear as in Fig. 7. The room temperature width is then always less than the 77°K width and increases less rapidly with concentration. The addition of In to Pb reduces the melting point of the alloy. This means that room temperature becomes an increasingly larger fraction of the melting point. The less rapid increase in the higher temperature linewidth is probably due to an increase in self-diffusion of the lead nuclei causing a motional averaging of the interactions responsible for the width.

The absorption width in pure lead is field-independent. Surprisingly, the linewidth in the alloys is strongly field-dependent, as shown in Figs. 5 and 6. The lines exhibit no apparent asymmetries. There are several field-dependent factors which may cause line broadening in powdered samples. They are (1) quadrupole

[24] J. Korringa, Physica **16**, 601 (1950).
[25] K. Asayama and J. Itoh, J. Phys. Soc. Japan **17**, 1065 (1962).

broadening, (2) macroscopic field inhomogeneities produced by the bulk magnetism of the sample,[26] (3) inhomogeneous isotropic Knight shift, and (4) anisotropic Knight shift. The first is absent since the nuclear spin of lead is one-half. The second broadening mechanism arises for materials with a large bulk magnetic susceptibility χ. In the presence of a steady field H, each particle in the sample is uniformly magnetized, nonetheless producing field inhomogeneities. This leads to an apparent broadening of the magnetic resonance line of the order[26] of $\Delta H = 3\chi H$. For Pb alloys $\Delta H \approx 0.03$ Oe, completely negligible compared to the linewidths involved.

The inhomogeneous isotropic Knight shift broadens the line because nuclei at various distances from surrounding solute atoms experience quite different electron densities and, therefore, different Knight shifts. The anisotropic Knight shift arises because of the large p character in the electronic wave functions at the Fermi-level and the deviation from local cubic symmetry at the Pb^{207} sites produced by adding In atoms.

The excess linewidth above the zero-field width thus must be attributed to either the inhomogeneous isotropic Knight shift, or to the anisotropic Knight shift, or to a combination of these. It does not seem possible, at the present state of the art, to unambiguously separate these two broadening mechanisms. Both Drain, for Ag-Cd, and Rowland, for a large number of Ag alloys, concerned themselves with the relative importance of these two sources of linewidth. Rowland dismissed the anisotropic Knight-shift broadening as an important source of linewidth in the Ag alloys on two main grounds. One was an unpublished calculation of Vosko, which showed that the anisotropic Knight shift would contribute to the width less than 10% of the change in Knight shift. The other was that the same calculated charge oscillations that successfully explained the line shifts (at least within a factor of 2) gave good agreement with the widths.

We favor the view that most of the field-dependent Pb^{207} width in Pb-In alloys arises from the anisotropic Knight shift on the following grounds: First, the fact that the shift is small and the width is large, although possible, has no theoretical justification for Pb-In and is in contrast to the Ag alloys or Ag-Cd system, where the shifts are comparable to the widths. Since the calculation of the charge oscillations in the Pb-In system has not been done, it is not possible to determine whether charge oscillations would, in fact, be large enough in magnitude to cause the observed field dependent widths, while at the same time producing only a small contribution to the shifts.

Second, the line shape predicted by Blandin and Daniel[16] for inhomogeneous Knight shift broadening is Gaussian above a few percent solute concentration. Rowland and Drain both observed Gaussian lines, whereas the 10% Pb-In line is as nearly Lorentzian at high fields as at low fields. Anisotropic broadening has previously been observed in tetragonal tin,[11] hexagonal cadmium,[27,28] rhombohedral mercury,[29] and hexagonal thallium.[12] In these pure metals, the observed effect consists of a characteristic asymmetric broadening proportional to the field. In contrast to these cases in which a preferred axis is determined by the crystal symmetry, the Pb-In system possesses no preferred axis, since the In atoms assume a variety of configurations with respect to the Pb nuclei. Our observation of little or no asymmetry in the resonance line shape is probably due to this lack of a preferred symmetry axis.[11] As far as we are aware, there have been no previous reports of anisotropic Knight-shift broadening in "cubic" alloys.

Third, the p character of the Pb conduction band is undoubtedly much greater than in Ag. The data given in this paper for the ratio of pseudodipolar to classical dipolar and of pseudodipolar to isotropic exchange confirm this point. Although a calculation similar to Vosko's Ag result is surely more difficult to make for Pb, for equal disruption of the cubic symmetry by the solute atoms, the larger p character in Pb would make the expected anisotropic Knight-shift broadening much larger in Pb than Ag.

The "zero-field" line in Fig. 6 represents the width in the absence of anisotropic or inhomogeneous Knight-shift broadening and this value minus the T_1 broadening is listed in Table I as the "corrected linewidth."

The natural abundance of Pb^{207} is 21%, hence, the pure lead classical dipolar width for like neighbors (all other isotopes have $I=0$) from Van Vleck's formula[30] is only 0.28 kc/sec. The contribution from the relatively short spin-lattice relaxation time, discussed above, is 0.50 kc/sec at 77°K. Since Pb^{207} is the only magnetic isotope, indirect exchange broadening is precluded, and the remaining part of the measured width in lead metal is attributed, as was done previously by Bloembergen and Rowland,[12] to a pseudodipolar interaction. The pseudodipolar contribution to the linewidth is then about 10 times that of the ordinary dipolar and, therefore, indicates a large amount of p character in the electronic wave functions at the Fermi level in lead.

An estimation of the amount of exchange narrowing may be made using the fact that exchange narrowing leaves the second moment of the line unchanged. In the absence of narrowing and relaxation time broadening, the pure lead line would be Gaussian, since only dipolar and pseudodipolar contribute. We observe a narrowed Lorentzian with a corrected linewidth $\delta\nu = 1.4$ kc/sec. From the relation between linewidths and second moments for Lorentzian and Gaussian lines discussed

[26] L. E. Drain, Proc. Phys. Soc. (London) **80**, 1380 (1962).

[27] T. J. Rowland, Phys. Rev. **103**, 1670 (1956).
[28] Y. Masuda, J. Phys. Soc. Japan **12**, 523 (1957).
[29] F. Reif, Phys. Rev. **102**, 1417 (1956).
[30] J. H. Van Vleck, Phys. Rev. **74**, 1168 (1948).

earlier, it is seen that, in general, the linewidth is narrowed by about a factor of $\frac{1}{2}$. Thus, for lead, exchange narrowing amounts to about 1.4 kc/sec.

An approximate evaluation of the exchange narrowing parameter, $A_{\mathrm{Pb-Pb}}$, may be made via a second-moment analysis of the pure lead Lorentzian line. For an exchange narrowed Lorentzian, the correct value for the second moment is obtained if the line is cut off at a frequency[12] $\nu_{co}=\lambda(\frac{1}{2}\pi)Z^{1/2}Ah^{-1}$, where $Z=12$, the number of near neighbors in a fcc lattice, and λ is a numerical constant of the order of unity. We find $\nu_{co}=7.5$ kc/sec, which yields $h^{-1}A_{\mathrm{Pb-Pb}}\approx 1.4$ kc/sec.

It is seen from Table I that the large increase in width at low fields is due to a combination of indirect spin exchange[12] and pseudodipolar coupling. The same factors are responsible for the shape change from Lorentzian toward Gaussian. In Table I, the classical dipolar was obtained from Van Vleck's second-moment formula. It is assumed that the T_1 contribution does not change much with alloying, since the change in Knight shift is small. However, a mechanism to shorten T_1 in the alloys may be available which does not involve the hyperfine interaction directly. Indium nuclei may be strongly relaxed to the lattice via quadrupole coupling. If this relaxation time is sufficiently fast then the lead nuclei may be effectively short-circuited to the lattice via their exchange interaction with the indium, thereby increasing the relaxation width in the alloys. A second mechanism which may be important in shortening T_1 is the coupling of nuclear spins to the lattice via the anisotropic Knight shift.

The "dipolar and pseudodipolar" second moment in the alloys is estimated by equating the ratio of the pseudodipolar to the classical dipolar second moment in an alloy to the same ratio in pure lead. The second moment due to exchange broadening is found as the remainder of the experimental second moment, which is approximately equal to the square of the corrected linewidth for the lower concentrations. The values for exchange broadening for the higher concentrations are not included in Table I because of the sensitivity of the result to the choice of the correction for the partly Gaussian line. Direct measurement of the second moment is also subject to large errors because of the poor signal to noise and the necessity of correcting for field-dependent contributions. Using a second-moment formula for near neighbors only,[9] and assuming a correction of about 20% for further lattice sites, yields a near-neighbor exchange constant for lead-indium, $h^{-1}|A_{\mathrm{Pb-In}}|=0.9$ kc/sec$\pm$0.4 kc/sec.

The contribution of pseudodipolar exchange to the second moment increases with concentration because the isotropic abundance of magnetic indium nuclei is much larger than that of magnetic lead nuclei. The numerical value of this exchange constant, however, should be only slightly dependent on concentration, because of the approximate equality of the g factors.

TABLE III. Dipolar, exchange, and pseudodipolar interaction between nearest neighbors, in kc/sec, for the lead-indium alloy system.

$\gamma^2hR_{\mathrm{Pb-In}}{}^{-3}/4\pi^2$	$\lvert A_{\mathrm{Pb-In}}\rvert h^{-1}$	$\lvert B_{\mathrm{Pb-In}}\rvert h^{-1}$
0.12	0.9	1.0

The value for the near-neighbor pseudodipolar exchange constant is calculated, using the data of Table I, to be $h^{-1}|B_{\mathrm{Pb-In}}|=1.0\pm0.2$ kc/sec. The values for $A_{\mathrm{Pb-In}}$, $B_{\mathrm{Pb-In}}$, and the classical dipolar constant for pure lead, are summarized in Table III. Bloembergen and Rowland have shown[12] that the ratio B_{ij}/A_{ij} has the order of magnitude of the hyperfine splitting ratio in corresponding p and s states times the relative amount of p with respect to s character of the wave function. Since the hyperfine splitting in a p state is an order of magnitude smaller than that in an s state, the ratio of the observed values $B/A\approx 1$, indicates that the amount of p character probably greatly exceeds the amount of s character of the electron wave functions at the Fermi surface in this alloy. This ratio for thallium metal, which lies next to lead in the periodic table and whose free atom has one less p electron, is[31] $B/A=0.1$. Quantitative conclusions are not possible without some knowledge of the complicated band structure of Pb-In.

The pseudodipolar and anisotropic Knight shift proceed via the same interaction between nuclear and electron spins. The coupling is brought about by that part of the conduction electron wave function which has non-s character. Large values of B compared to A, and compared to classical dipolar, is considered evidence for very large p character in the wave functions near the Fermi level in lead-indium alloys, and is consistent with the observation of anisotropic Knight-shift broadening.

V. SUMMARY

The fractional change in the Knight shift of Pb^{207} upon the addition of indium (Fig. 3) is found to be small ($\Delta k/k=1.1\%$ at. 20% In), while the linewidth (Fig. 4) increases rapidly. The shift as a function of concentration is linear to 50% In. An estimate of volume effects, assuming a free-electron model, indicates that the changes in volume associated with alloying may cause appreciable frequency shifts. The absence of accurate knowledge of the volume dependence of the Knight shift precludes the possibility of a definite conclusion regarding the existence of charge oscillations in the lead-indium system.

From the temperature dependence of the linewidth, the spin-lattice relaxation time is found to be $T_1=3.6\times10^{-4}$ sec at 77°K. The high In-concentration line-

[31] Yu. S. Karimov and I. F. Shchegolev, Zh. Eksperim. i Teor. Fiz. 41, 1082 (1961) [translation: Soviet Phys.—JETP 14, 772 (1962)].

widths seem to be reduced at 300°K by motional narrowing. The observed linewidth is separated into its separate contributions. The linear field dependence of the width (Fig. 5) is attributed primarily to anisotropic Knight-shift broadening, although inhomogeneous isotropic Knight-shift broadening is not excluded. The rapid increase of the zero-field linewidth upon alloying is attributed to a combination of indirect spin exchange and pseudodipolar coupling. These interactions are also responsible for the line shape change from Lorentzian toward Gaussian. The exchange-only second moment yields a value for the near-neighbor exchange constant for unlike nuclei $h^{-1}|A_{\mathrm{Pb-In}}|=0.9\pm0.4$ kc/sec. The pure lead line is Lorentzian due to exchange narrowing. A second-moment analysis yields a value for the strength of the interaction between like nuclei, $h^{-1}|A_{\mathrm{Pb-Pb}}|=1.4$ kc/sec. The pseudodipolar exchange constant is found to be $h^{-1}|B_{\mathrm{Pb-In}}|=1.0\pm0.2$ kc/sec. Large values for the ratio $B_{\mathrm{Pb-In}}/A_{\mathrm{Pb-In}}$ and the ratio of pseudodipolar to classical dipolar indicate that the amount of p character probably greatly exceeds the amount of s character in the electron wave functions at the Fermi surface in these alloys, and is consistent with the observation of anisotropic Knight-shift broadening.

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Infrared Lattice Vibrations and Dielectric Dispersion in Corundum

A. S. BARKER, JR.
Bell Telephone Laboratories, Murray Hill, New Jersey
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Room-temperature reflectivity measurements in the wavelength range 1 to 140 μ have been made on corundum and ruby. Classical oscillator analysis of the data shows that the optical lattice modes with dipole moment vibrating perpendicular to the C axis occur at 15.7, 17.6, 22.6, 26.0 μ. Those vibrating parallel to the C axis occur at 17.1 and 25.0 μ. The line-widths and strengths are reported. Many forbidden modes are observed. Two of these can have a strength which is comparable to the allowed modes but which is sensitive to surface treatment. Symmetry arguments show that these strong forbidden modes are the A_{1u} (forbidden) phonon branches picking up dipole moment as a result of shear strain.

INTRODUCTION

THE infrared lattice-vibration spectra of corundum (α-Al_2O_3) and chromium-doped corundum (ruby) have been studied by several workers since the original work of Coblentz[1] in 1908. Krishnan has reported on the Raman spectrum of alumina[2] and summarized the infrared results to 1947.[3] In spite of the large body of experimental results listed by Krishnan, and some more very recent and extensive infrared measurements,[3,4] there are several ambiguities and anomalies in the frequencies assigned by the various authors. Also, all of the infrared active modes predicted by group theory have not been previously identified experimentally.

The present work was undertaken to discover all the normally allowed infrared vibration modes of the α-Al_2O_3 lattice and to obtain the optical constants throughout the region of the lattice vibrations. Polarized reflection spectra were made from 1 to 140 μ and these spectra were analyzed using Kramers-Kronig dispersion analysis and classical oscillator formulas.[5]

Four infrared modes active for $E\perp C$ axis and two active for $E\|C$ axis are predicted by the symmetry of the α-Al_2O_3 lattice where E is the electric field vector of the infrared beam. These modes are clearly detected in the present experiments and are discussed below. Anomalously low-frequency modes at 194 cm^{-1} and 244 cm^{-1} were reported by Parodi,[6] and have been used by several authors to explain fine structure which appears in the luminescence spectrum of ruby.[3,7,8] No infrared modes were found at these frequencies in the present work. As might be expected, the measurements show that the presence of chromium impurities even up

[1] W. W. Coblentz, *Supplementary Investigations of Infrared Spectra* (The Carnegie Institution, Pub. No. 97, Washington, 1908), p. 17.
[2] Various names are used in the literature to describe pure α-Al_2O_3 crystals. Some of these are: Corundum, sapphire, and alumina (or better-α-alumina).
[3] R. S. Krishnan, Proc. Indian Acad. Sci. **26A**, 450 (1947).
[4] A. Mitsuishi, H. Yoshinaga, S. Fujita, and Y. Suemoto, J. Appl. Phys. (Japan) **1**, 1 (1962).
[5] W. G. Spitzer and D. A. Kleinman, Phys. Rev. **121**, 1324 (1961).
[6] M. Parodi, Compt. Rend. **205**, 906 (1937).
[7] R. A. Ford and O. F. Hill, Spectrochim. Acta, **16**, 493 (1960).
[8] It seems likely that phonons near the zone boundaries will contribute most strongly to the luminescence structure, thus, infrared and Raman frequencies may not be very useful in fitting such structure.

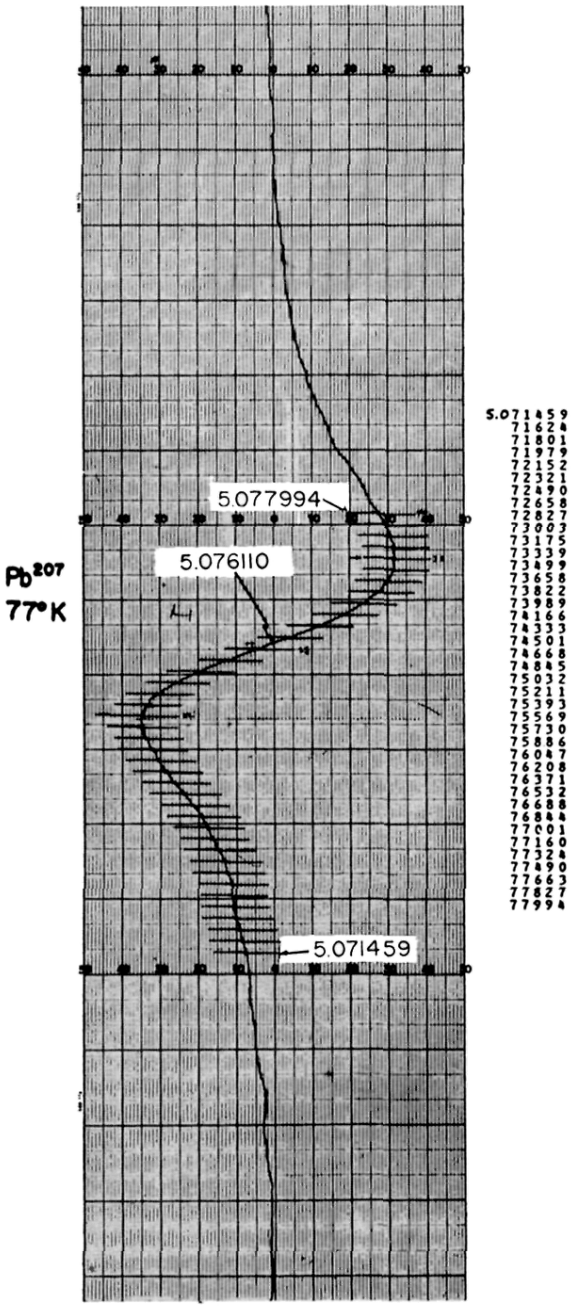

FIG. 2. Nuclear magnetic resonance curve of Pb^{207} at 77°K showing frequency markers about 200 cps apart. Frequency values corresponding to each marker are automatically recorded.