width in fact becomes temperature-independent at $\Delta H=0.1$ G. A simple linewidth measurement of the proton resonance in a water sample of the same dimensions as the sodium sample showed the field inhomogeneity over the sample to be about 0.1 G. The field was so inhomogeneous over the small sample because the ratio of the magnet gap to the pole cap diameter was 5:12; the large gap was required in order to fit in the rather bulky microwave cavity and the glass Dewars. Thus our data may not be compared to Yafet's calculations below about 35°K, where the measured linewidths is 0.4 G. We can say in defense of our poor homogeneity that even if Yafet's calculations are correct only down to 20°K the linewidth would be on the order of $\frac{1}{10}$ our present limit. Thus a substantial improvement in homogeneity would not extend our range of valid data very significantly. The calculated relaxation times in the hydrogen temperature region are long enough to allow a direct measurement of T_1 by transient techniques.

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Absence of Pronounced Quadrupole Effects in the Nuclear Resonance of In^{115} in a Noncubic Environment*

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The nuclear magnetic resonance of In^{115} has been observed throughout the cubic phase of Pb-In alloys, at 77 and 300°K. The Knight shift is 0.86% and is essentially unchanged with composition. The linewidths increase rapidly with In concentration, probably mostly due to pseudodipolar interaction. The average electric field gradient at a In^{115} nucleus for any configuration of Pb neighbors is about $q\sim3\times10^{22}$ cm^{-3}, about 20 times smaller than for Cu having a Zn second neighbor in the fcc Cu lattice. The small value of the field gradient is discussed in terms of the behavior of the charge oscillations, and is related to the small change in Knight shift for Pb^{207} in these same alloys.

I. INTRODUCTION

THE nuclear electric-quadrupole moment interacts with the electric field gradient at the site of the nucleus. In a position of cubic symmetry, the electric field gradient vanishes and there is no quadrupole interaction. In the liquid phase of a metal, atomic motion is usually sufficiently rapid to average out the field gradients. Knight[1] pointed out that, in some cases, strong quadrupole interactions may obliterate the nuclear magnetic resonance (NMR) signal of a quadrupolar nucleus in the noncubic lattice of the pure metal, but that the nucleus may still exhibit a strong NMR signal when substituted in the cubic environment of another metal. For example, in pure orthorhombic Ga, the nuclear magnetic resonance has been observed in the liquid phase only. However, when Ga is substituted in the face-centered cubic lattice of Cu, the cubic environment substantially reduces the quadrupole coupling for many of the Ga atoms and the nuclear magnetic resonance is observable. Knight suggested that it might be possible to make suitable alloys of other metals for which the resonances are unobservable in the pure state.

Following this suggestion, one of the present authors[2] observed a strong NMR signal of In^{115} substituted in the cubic lattice of a 95% Pb−5% In alloy. If the indium is randomly distributed throughout the lattice, about one-half of the indium atoms have only lead for first, second, and third nearest neighbors. The intensity of the In^{115} resonance compared to the Pb^{207} in this alloy led to the conclusion that *these* atoms were observed, together with some of the satellite intensity. An alternative possibility is that all In^{115} nuclei participate in the resonance but that some of the satellite intensity is smeared out.

In order to distinguish between these possibilities the

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In^{115} resonance was looked for in other alloying proportions. Very surprisingly, the In^{115} resonance remained observable with almost no change in intensity per atom throughout the cubic lead phase.[3] Figure 1, for example, shows the observed room-temperature Pb^{207} and In^{115} NMR absorption derivatives in alloys containing 0.5 at.% In and 35 at.% In. There is no essential difference in the In^{115} resonance at 77°K in any of the alloys studied.

Since the start of this research, the pure quadrupole resonance of In^{115} in tetragonal indium metal has been discovered[4,5] with a room-temperature quadrupole coupling constant of approximately 30 Mc/sec. The high-field nuclear resonance of In^{115} in indium metal has also been observed,[6,7] but with extremely large quadrupole effects in agreement with the known quadrupole coupling constant in the tetragonal lattice. The In^{115} resonance has also been observed in liquid indium,[8] but here the rapid motion washes out quadrupole interactions. Nuclear magnetic resonance studies[9] of In^{115} in an unstrained single crystal of InSb revealed negligible quadrupole interactions, due to the high symmetry of the zinc blende lattice of InSb. Thus, none of these other results is directly comparable with our surprising observation of the absence of pronounced quadrupole effects in the noncubic environment of the nondilute Pb-In alloy.

In Sec. II we present the experimental data on the In^{115} NMR absorption derivatives linewidths, centers and relative intensities as a function of concentration of In in Pb, magnetic field, and temperature. In Sec. III, we discuss the significance of the observation of the In^{115} resonance in the "noncubic" environment of the high indium concentration alloys in lead. We relate this absence of pronounced quadrupole effects to the small changes in Knight shift in the Pb^{207} resonance in these same samples discussed in a preceding paper.[10]

II. EXPERIMENTAL METHODS AND RESULTS

Indium, a column III element, is dissolved in lead, a column IV element. Lead is a face-centered-cubic metal with melting point of 327°C. All measurements were made in the cubic phase which persists up to about 68 at.% In. In^{115} is 96% abundant, has a nuclear spin $I=9/2$, a large nuclear magnetic dipole moment

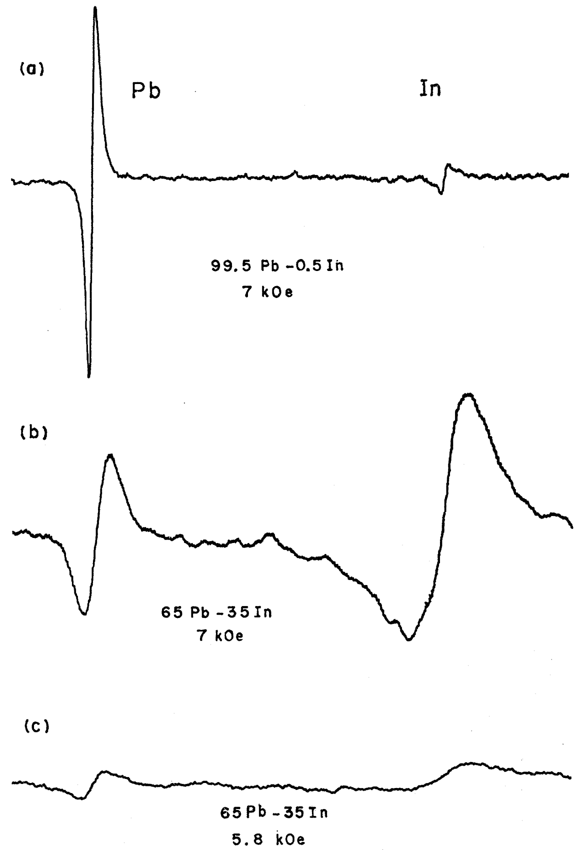

FIG. 1. First derivative of the room-temperature nuclear magnetic resonance absorptions of Pb^{207} and In^{115} in (a) 99.5% Pb−0.5% In at 7.0 kOe, (b) 65% Pb−35% In at 7.0 kOe and (c) 65% Pb−35% In at 5.8 kOe.

(5.5 n.m.), and a large electric quadrupole moment (1.16 b).

All of the resonances were observed at both 77° and 300°K with a Varian wide-line spectrometer. The experimental techniques and the preparation of the alloys have been discussed previously.[10,11] Typical resonances are shown in Fig. 1. Since the Pb^{207} and In^{115} resonance differ in shape and width, it is somewhat misleading to compare the recorded absorption derivatives in order to determine relative intensity. Instead, a point by point integration was made of each resonance, and the relative areas of the resulting absorption curves were compared. The assumption was made that the absorption is zero in the wings when the derivative is zero. This assumption has the effect of ignoring flat wings, and thus underestimating the contribution of In^{115} satellites.

If we make the reasonable assumption that we are observing all of the Pb^{207} nuclei, then a comparison of the relative intensities of the Pb^{207} and In^{115} resonances *in the same sample* gives an indication of the portion of

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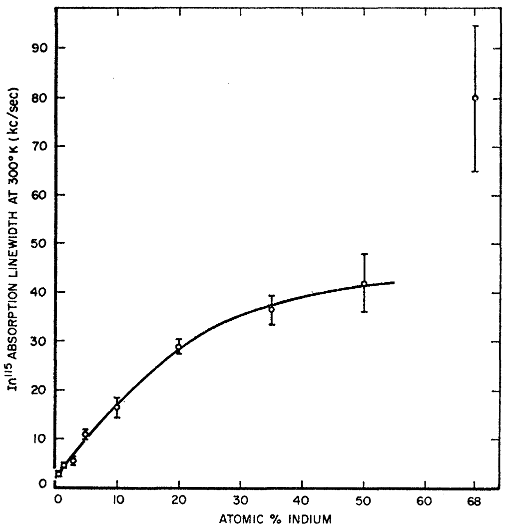

FIG. 2. In^{115} absorption linewidth versus In concentration at 300°K and 7.0 kOe.

the possible In^{115} resonance we are observing. This is independent of frequency, filling factor, and other experimental parameters, provided only that there is no modulation broadening. This comparison showed that, with the exception of the 68% In sample, there was almost no change in intensity per atom of the In^{115} throughout the cubic lead phase. The absolute intensity of the In^{115} in any of these samples corresponded to about 10 to 20% of that possible, in good agreement with the intensity expected from the central transition alone. We conclude that we are observing only the central line of essentially all In^{115} nuclei in the alloys, at both 77 and 300°K.

There is virtually no second-order quadrupole shift at 7.0 kOe or above. For the 35% In sample, Fig. 1[(b) and (c)] shows the room-temperature resonance absorption derivatives of In^{115} and Pb^{207} at 7.5 and at 5.8 kOe. The In^{115} resonance at the lower field shows some sign of second-order broadening. Any shift in center between these two In^{115} resonances (normalized to 5.8 kOe) is less than 1 kc/sec.

The presence of substantial ordering or clustering would of course change the main result of this paper, that we are observing only small quadrupole effects in a *noncubic* environment. An x-ray study[12] of the 20% In and the 35% In sample used in this research revealed no short-range order. The short-range order parameter in the ith shell around an A atom is defined as $\alpha_i = 1 - P_{AB_i}/X_B$, where P_{AB_i} is the probability of a B atom in the ith shell around an A atom, and X_B is the mole fraction of B. If α_1 was ≈ -0.05 or greater in magnitude, it would have been detected. Clustering ($\alpha_1 > 0$) was not checked. A short-range order parameter equal to 0.14 was suggested recently.[13] Even if the short-range order were this high, fewer than 1% of the In would be in cubic environments in the 50-50 alloy.

The In^{115} linewidth as a function of In concentration is shown in Fig. 2. The increase in the In^{115} linewidth with In concentration can be understood if the pseudodipolar interaction is assumed to be about 10 times the ordinary dipolar. The pseudodipolar interaction was found to be about 10 times the dipolar for the Pb^{207} linewidth[10] in these same samples. No careful studies of the field dependence of the linewidth was made—it is believed that a combination of second-order quadrupolar broadening at the lower fields, and anisotropic and inhomogeneous isotropic Knight shift broadening[10] at the higher fields could be important. The 68% In point does not fall on the smooth curve in Fig. 2. From the Pb^{207} Knight shifts, we had previously[10] concluded that this alloy was in a two-phase region.

The resonance center is largely independent of concentration, occurring at 6.586±0.001 Mc/sec at 7000 Oe. This corresponds to a Knight shift of 0.86±0.01%, which is close to the value found in the tetragonal phase of pure In[7] (0.82±0.04% for the isotropic shift), or in the liquid phase of In metal[8] (0.79±0.03%, the ± taking into account the variation with temperature, and chemical shifts). There is no *a priori* reason for expecting this close agreement.

III. DISCUSSION

The most important result of this work is the observation of the In^{115} resonance in the "noncubic" environment of nondilute Pb–In alloys. This result was unexpected in view of the large quadrupole moment of In^{115} and the observations of Rowland and Bloembergen[14] on the Cu–Zn system. In that case Cu was the solvent, Zn the solute. In pure Cu, the Cu^{63} resonance is reduced by cold working to 0.4 times the intensity in the well-annealed metal. An average electric field gradient of $q = 1.6 \times 10^{22}$ cm^{-3} produced by cold working accounts for this observation. As Zn is added to Cu, the Cu^{63} intensity is further reduced until the resonance is unobservable for Zn concentrations of more than about 20%. Rowland concluded that no Cu^{63} nuclei were observed when Zn destroyed the cubic symmetry in the first or second coordination shell. Rowland estimated that a gradient $q > 1.6 \times 10^{23}$ cm^{-3} is needed to account for the loss of Cu^{63} nuclear contributions to the NMR line for Zn nearest and second-nearest neighbors. In a recent direct measurement, Redfield[15] showed that the quadrupole frequency for second neighbors was 1980 kc/sec (corresponding to $q = 7 \times 10^{23}$ cm^{-3}), and for first was probably greater than 5 Mc/sec, consistent with Rowland's estimate.

In order to contrast the Pb-In results with the Cu-Zn work, it may be meaningful to think of In as the solvent,

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TABLE I. Average electric field gradients at nuclei in metals.

	Cold worked Cu	Cu Having Zn 2*d* neighbors	In in In-Pb	Al in Al-Mg or Al-Zn alloys
$q(cm^{-3})$	1.6×10^{22}	70×10^{22}	3×10^{22}	17×10^{22}

Pb as the solute. We do not observe the In in the dilute region (high In concentration) due to the tetragonal structure. But, consider a hypothetical cold-worked cubic In metal in analogy to the cold-worked cubic Cu metal. As the solute (Pb) is added, the In^{115} intensity per atom would be expected to decrease. Thus, for example, we would expect the In^{115} resonance in the 50% In–50% Pb alloy to be unobservable (unless there is substantial clustering or ordering, which does not seem to be the case). In fact, the resonance intensity in the 50% In–50% Pb alloy is very large, corresponding to the observation of the central transition of *all* the In^{115} nuclei. Using a method described by Rowland,[16] and assuming we have no more second-order effects than discussed in Sec. II of this paper, we obtain $q<4.6\times10^{22}$ cm^{-3} for the average electric field gradient at a In^{115} nucleus for any configuration of Pb neighbors. From the fact that the satellites do not contribute to the observed lines, we find $q>1.4\times10^{22}$ cm^{-3}. Thus we can take $q\approx3\times10^{22}$ cm^{-3} as the average gradient at the In nuclei, which is comparable to the field gradient in pure cold-worked Cu, and is 20 times smaller than that found for Cu having Zn second-nearest neighbors, as is shown in Table I.

Kohn and Vosko[17] have explained the magnitude of the field gradients at the Cu site due to various solute atoms[14] on the basis of a redistribution of the conduction electron charge density near the solute.[18] The reduction in Cu NMR absorption intensity with increasing solute concentration was taken as confirmation of a long-range oscillatory behavior of the electron density. This same type of oscillatory behavior was shown to be responsible for the change in Knight shifts in silver,[19,20] cadmium,[20] and the alkali metals.[21]

In the case of Pb-In, it has already been pointed out[10] that the changes in Knight shift of the Pb^{207} upon the addition of In are small. No definite conclusion could be reached as to the importance of the charge oscillations in the lead-indium system. In any case size effects are probably too big to be neglected. We have not yet made a quantitative estimate of the field gradients. A possible explanation for both the small change in Pb^{207} Knight shift and the absence of In^{115} pronounced quadrupole effects is that the charge oscillations are greatly damped or that they oscillate rapidly and are effectively averaged out. It might then be appropriate to say that the In atoms in the cubic Pb phase screen themselves to "look almost like" Pb atoms, as far as Knight shifts and quadrupole effects are concerned. Of course, the anisotropic Knight shift broadening[10] depends on the In disrupting the cubic symmetry of the lattice so this description is not completely adequate.

It is also interesting to compare the Pb-In work with Webb's measurements[22] on Al-Zn and Al-Mg. For both Pb^{207} and Al^{27} only small changes in the Knight shift are observed. The average electric field gradient q at the site of an aluminum nucleus which is nearest neighbor of a solute (Zn or Mg) atom is found by Webb to be 17×10^{22} cm^{-3}. This is an intermediate value between In-Pb and Cu-Zn. It appears as if the effective valence difference between adjacent metals having higher group (or atomic) valences is less than for those with lower valences.

The angular correlation of the γ-γ cascade of In^{111} in thin layers has been measured[23] as a function of In concentration. This experiment shows a relatively large increase in anisotropy in going from almost pure lead to Pb-1.5% In. Kaiser attributes this increase to the electric field gradients at an indium atom due to its nearness to other indium atoms. He then compares his result to Bloembergen and Rowland's observation of the rapid loss in Cu NMR intensity upon addition of Zn. Our results show that the In-Pb result should not be compared to the Cu-Zn work. However, it is possible that an increased quadrupole interaction, reflected in the anisotropy, is associated with a first-order splitting of the satellites.

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