

Nuclear Magnetic Resonance in Lead Alloys*

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(Received 31 January 1964)

The Pb^{207} nuclear magnetic resonance has been measured in a series of lead base primary solid solutions containing Cd, In, Sn, Sb, Hg, Tl, and Bi as solutes. The central resonance frequency of Pb^{207} shifts in proportion to the solute concentration and in the opposite direction to be explained by impurity charge screening of the Thomas-Fermi type. The fractional change in Knight shift for all solutes is small $\Delta k/k \approx 0.05 c$. The important parameter in determining the change in Knight shift seems to be the difference in valence between the impurity atoms and the lead atoms. The absorption linewidths broaden rapidly upon the addition of solute. In the absence of a quantitative calculation it is not possible to determine if the small shifts, large widths, and small quadrupole effects of In^{115} are consistent with the theory of long-range oscillations of electronic charge. However, there is evidence that this theory may be capable of explaining our data.

THE nuclear magnetic resonance (NMR) of Pb^{207} has been accurately measured in a series of lead base primary solid solutions containing second (Cd, In, Sn, Sb) and third (Hg, Tl, Bi) long period solutes. This is the first report of comprehensive Knight shift measurements on a polyvalent nontransition metal matrix. It is especially interesting to see if the theory¹ developed by Friedel, Blandin, and Daniel concerning the long-range oscillation of electronic charge density around impurity atoms in monovalent and divalent metals is capable of explaining our data for a polyvalent material. The major conclusion is that, in qualitative agreement with the Friedel theory, the valence of the solute is the controlling factor in the change of Knight shift with solute concentration.

Figure 1 shows the change in Pb^{207} resonance frequency from pure lead metal at 7 kOe and 300°K as a

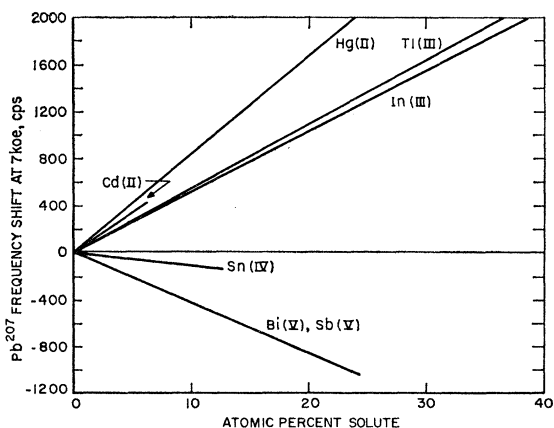


FIG. 1. Change in Pb^{207} Knight shift versus solute concentration at 300°K.

function of solute concentration.² The central resonance frequency of Pb^{207} shifts in proportion to the solute concentration (c). The shifts are in the opposite direction to be explained by impurity charge screening of the Thomas-Fermi type. The fractional change in

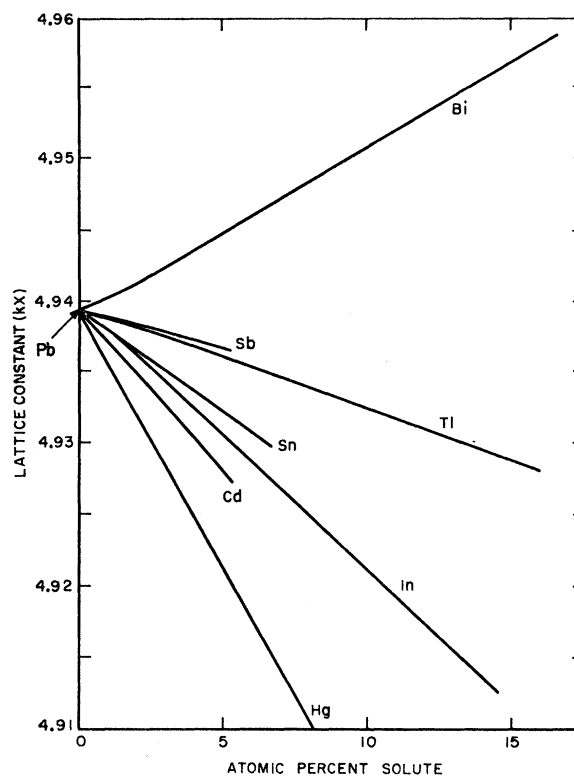


FIG. 2. Lead solid-solution lattice spacings at 20°C. After Tyzack and Raynor (Ref. 3).

* Some of the material contained herein is given in a Ph.D. thesis submitted by R. J. Snodgrass to the University of Maryland.

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¹ J. Friedel, *Phil. Mag.* 43, 153 (1952); A. Blandin, E. Daniel, and J. Friedel, *ibid.* 4, 180 (1959); A. Blandin and E. Daniel, *Phys. Chem. Solids* 10, 126 (1959).

Knight shift for all solutes is small $\Delta k/k \approx 0.05 c$. The experimental points were omitted for clarity. The experimental error is of the order of the separation of the In and Tl lines in Fig. 1.

² The Pb^{207} -In data was described in detail in R. J. Snodgrass and L. H. Bennett, *Phys. Rev.* 132, 1465 (1963).

The lead solid solution lattice spacings³ for the same solutes are shown in Fig. 2. A comparison of Figs. 1 and 2 shows that the frequency shifts partially correlate with lattice parameter changes. However, Bi and Sb give identical changes in Knight shift while the former expands and latter contracts the Pb lattice. Tl and In are more widely separated in lattice spacings than in resonance frequencies. Sn causes a larger change in lattice parameter than Tl, but a much smaller change in Knight shift (and in the opposite direction) to Tl. The correlation of the Knight shift results with Pauling or Goldschmidt radii is not good at all. From this we conclude that "size effects" are not the controlling factor in determining the Knight shift in these alloys. It is not surprising that there is partial correlation with lattice parameter data since the lattice spacing reflects not only size effects, i.e., misfit between solvent and solute, but also valence effects. The important parameter seems to be the difference in valence between the impurity atoms and the lead atoms. However, superposed on this may be a slight period dependence associated with impurities of equal valence which belong to different periods of the periodic table.⁴ A pure valence effect would perhaps predict zero shift for tin. The observed shift is indeed small. Similarly, the small deviation of Cd and In from Hg and Tl, respectively, may be a period effect. However, Sb does not deviate from Bi.

The absorption linewidths are shown in Fig. 3. They broaden rapidly upon the addition of solute. It was shown previously² that the Pb^{207} resonance depends linearly upon the applied magnetic field for the Pb-In alloys. Since the line shapes are predominantly Lorentzian, especially for the dilute alloys, it is difficult to estimate second moments for comparison with theory. The anomalously large breadth due to Bi may be associated with its large magnetic moment, high-spin and high-isotopic abundance, together with a large exchange or pseudoexchange coupling constants. It is also possible that T_1 effects enter.

In conclusion, it seems somewhat surprising that the change in Pb Knight shift is so small, while the increase in widths is large. We believe the small change in Knight shift and the absence of pronounced quadrupole effects⁵

³ C. Tyzack and G. V. Raynor, *Acta Cryst.* **7**, 505 (1954).

⁴ F. J. Blatt, *Phys. Rev.* **108**, 285 (1957).

⁵ L. H. Bennett and R. J. Snodgrass, *Bull. Am. Phys. Soc.* **7**, 228 (1962), and to be published.

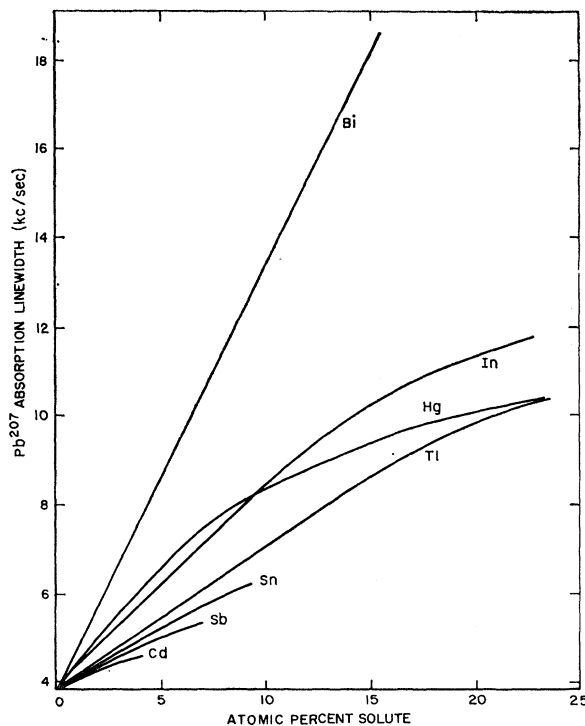


FIG. 3. Pb^{207} absorption linewidths versus solute concentration at 300°K and 7 kOe.

at the quadrupolar In^{115} nucleus in Pb-In alloys are related. In the absence of a quantitative calculation it is not possible to determine if the small shifts, large widths, and small quadrupole effects of In^{115} are consistent with the theory of long-range oscillations of electronic charge. However, there is evidence that this theory may be capable of explaining our data. (1) The shifts correlate with valence. (2) The sign of the shifts is in the opposite direction to be explained by Thomas-Fermi screening. (3) The absorption linewidths are field-dependent. This might also be due to anisotropic Knight-shift broadening, but we have not excluded inhomogeneous isotropic Knight-shift broadening.

ACKNOWLEDGMENTS

We are very grateful to D. P. Fickle for preparing the samples and to C. J. Bechtoldt for x-ray measurements.