

NUCLEAR MAGNETIC RESONANCE IN INTERMETALLIC COMPOUND $\text{Na}_{15}\text{Pb}_4$

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NEGATIVE Knight shifts have been reported by many workers¹⁻⁴ in intermetallic compounds. Shulman *et al.*³ observed negative shifts in the intermetallic compounds V_3Ga , V_3Sn and Nb_3Sn at the sites of Ga and Sn nuclei, although the relative Knight shifts for Ga and Sn nuclei in pure metals are positive.⁵⁻⁶ Both Gallium and Tin are in body-centred cubic site of Wolfram type in which they are surrounded by twelve equidistant near neighbours of Vanadium and Niobium atoms respectively. The negative shift observed at the site of X in V_3X (where X = Ga, Sn, As, Sb and Si) has been qualitatively explained by Glogston and Jaccarino⁷ on the assumption that *ns* wave functions belonging to the X site form a very narrow band lying far below the Fermi surface, whereas *np* wave functions lie sufficiently close to the Fermi surface so that they are strongly admixed with the Vanadium bands. Since *ns*-electrons are far below the Fermi surface, this band will be filled and cannot contribute to the observed shifts. Any polarization of the compound will consequently represent a partial polarization of *np*-electrons. However, the *p*-electrons have no contact hyperfine interaction. Exchange interaction between *np*-electrons and the inner *s*-electrons of the completely filled shells of X-atoms should therefore exist to explain the negative shifts for X-atoms in V_3X compounds.⁷

A similar situation has been discussed by Cohen *et al.*,⁷ who have taken into account both the contact hyperfine interaction due to *s*-electrons and the effect of core polarization by *p*-electrons to compute the theoretical value of Knight shift in sodium and lithium more accurately. As pointed out by them, the core polarization contributed negatively to the Knight shift.

NMR study of the intermetallic compound $\text{Na}_{15}\text{Pb}_4$ having a body-centred cubic structure type D8_6 , belonging to a space group $143d^0$ was undertaken. This compound is almost similar to V_3X system in structure

in the sense that each lead atom (like X-atom in V_3X compound) is isolated from the other, and is completely surrounded by twelve sodium neighbours.

The alloy was prepared by melting the requisite amounts of sodium and lead at about 500°C . in vacuum. It was powdered to have a particle size less than the skin depth at the operating frequency. The X-ray powder pattern obtained corresponds to the one reported by Zintl and Harder¹⁰ and later confirmed by Shoemaker *et al.*¹¹ for $\text{Na}_{15}\text{Pb}_4$.

The NMR measurements were made on a wide-line spectrometer of the Bloch type, the working field being 8.0 kilogauss for Pb^{207} . Na^{23} spectra have been recorded at 9.0, 6.8 and 4.5 kilogauss.

The relative Knight shift of Pb^{207} in the alloy has been found to be negative, though the corresponding shift in pure metal is positive, the values being respectively -0.36 ± 0.01 and $+1.45 \pm 0.01$ per cent. with reference to Pb^{207} in solid lead nitrate where its resonance occurs at the highest magnetic field.¹²

In a compound like $\text{Na}_{15}\text{Pb}_4$ where an atom (Pb) is surrounded by twelve foreign neighbours, extending the band structure proposed by Clogston and Jaccarino⁷ to this case, and taking the atomic configuration of lead as $6s^26p^2$, one can safely presume that the $6s$ wave functions at the site of lead atoms form a narrow band lying far below the Fermi surface, whereas the $6p$ wave functions lie sufficiently close to the Fermi surface and are strongly admixed with the sodium bands. On this model a negative shift for Pb^{207} in the alloy can be easily understood.

The experimental root mean square linewidth for Pb^{207} has been found to be 0.85 ± 0.08 gauss which is close to the computed linewidth of 0.64 gauss due to dipolar interaction alone. Relatively small contribution to the linewidth by other broadening mechanisms can be understood in this type of structure where lead nuclei are isolated from one another by low Z-sodium nuclei.

Na^{23} NMR spectrum in this compound shows two lines, a broad and asymmetric one superposing the other narrow line (Fig. 1). It thus indicates the existence of two non-equivalent sodium nuclei, Na (I) and Na (II), in the alloy. Further it has been observed that the narrow line [say due to Na (II)] is split into three first-order quadrupole components (Fig. 2), one corresponds to undeviated central component $\nu_{+1/2 \rightarrow -1/2}$ and the other satellite pair, corresponding to the transitions $\nu_{-1/2 \rightarrow -3/2}$ and $\nu_{3/2 \rightarrow 1/2}$ symmetrically placed about the central component. The spectra have been recorded at three different fields, 9.0, 6.8 and 4.5 kilogauss to verify the

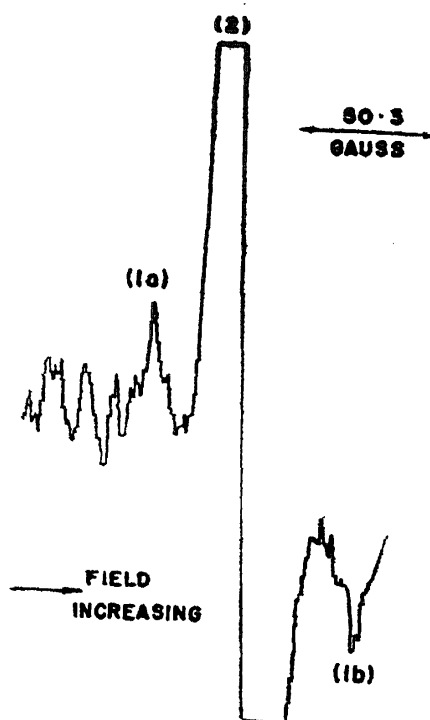


FIG. 1. Na^{23} NMR Absorption spectra corresponding to $2 \nu_{+1/2} \rightarrow \nu_{-1/2}$ transition in the alloy at 5 Mc./sec. (1 a) and (1 b) are the maximum and minimum respectively of the line due to Na (I). (2) is the line due to Na (II).

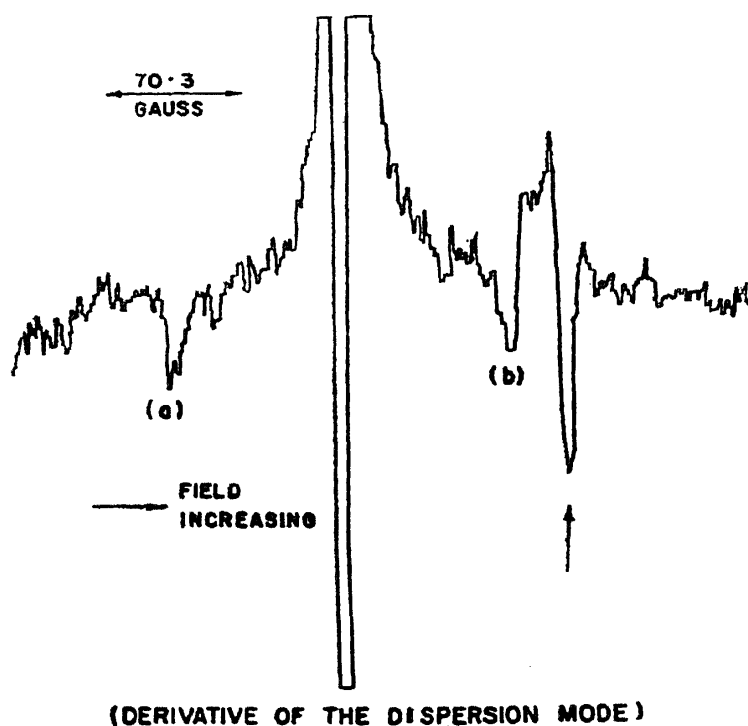


FIG. 2. The complete spectrum of Na^{23} [Na (II)] in the Alloy at 9.9 Mc./sec. The line indicated by the arrow is Al^{27} signal from the NMR probe. (a) and (b) are the satellite pairs corresponding to $\nu_{-1/2} \rightarrow \nu_{-3/2}$ and $\nu_{3/2} \rightarrow \nu_{1/2}$ transitions. The line due to Na (I) is merged in the central component of Na (II).

field independence of the satellite pair separation. The width of the broad line [due to Na (I)] has been found to be inversely proportional to the steady

field indicating that the broadening is due to the second-order quadrupole interaction. Assuming vanishing asymmetry parameter ($\eta = 0$), the quadrupole coupling constants at the site of Na (I) and Na (II) have been calculated. They are respectively 1.8 ± 0.1 and 0.39 ± 0.03 Mc./sec.

X-ray investigation¹⁰⁻¹¹ also reveals the existence of two non-equivalent sodium atoms with the abundance ratio of 1:4. The relative intensity consideration of the NMR lines qualitatively indicates that Na (II) corresponds to atoms with higher abundance ratio. It may also be pointed out that at 6.8 kilogauss, the centre of gravity of the line due to Na (I) has been found to have a relative Knight shift of $+0.05 \pm 0.01$ per cent. whereas the line due to Na (II) shows a very small Knight shift of $+0.009 \pm 0.003$ per cent. with reference to the same in sodium chloride.

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