FEATURES OF THE BAND STRUCTURE OF ISOVALENT CADMIUM
ALLOYS DEDUCED FROM NMR DATA

V. V. Zhukov

A study is made of the behavior of the components of the Knight shift tensor in alloys of cadmium with mercury and magnesium in a wide range of concentrations and temperatures. It is shown that the high sensitivity of the shift of the NMR frequencies to various effects in the hexagonal \( \alpha \) phase of the cadmium alloys is a consequence of their specific band structure. To analyze the Knight shift in the alloys, results of calculations of the electron spectrum and the Knight shift for pure cadmium in the model of the non-local Stark–Falicov pseudopotential were used. The nature and features of the rearrangement of the spectrum as a result of the alloying are determined from NMR data.

The theoretical analysis of the electron spectrum and wave functions of pure cadmium [1-4] have made it possible to understand the anomalously strong temperature dependence of the isotropic \( (K_{iso}) \) and anisotropic \( (K_{an}) \) components of the Knight shift tensor of this metal [5-9].

It was found [1, 2] that the Knight shift in cadmium is due to a small number of states whose population is very sensitive to a change in the splittings in the electron energy spectrum [10, 11]. When the temperature is raised, the lattice vibrations lead to a reduction of the structure factor in the Fourier components of the pseudopotential. The corresponding changes in the splittings explain the behavior of the components of the shift tensor, i.e., the Knight shift in cadmium makes it possible to investigate experimentally features of its band structure in a wide range of temperatures [2]. It is natural to expect the Knight shift to reflect the rearrangement of the electron spectrum in cadmium-based alloys as well.

In the preceding studies [12, 13], attempts were made to use the Knight shift to analyze the electron structure of the isovalent alloys Cd–Mg and Cd–Hg. The change in the electron spectrum of the alloys was represented in a simplified form as a sum of two effects — a change in the mean value of the pseudopotential form factor (the virtual-crystal approximation [11]) and a smearing of the spectrum due to the random distribution of the potential over the lattice sites. It was shown that both mechanisms make comparable contributions to the behavior of the Knight shift. However, since the model of a local pseudopotential is not valid for the description of the band structure of the cadmium matrix, it was not possible to obtain reliable quantitative estimates.

The improvements made in the present paper are achieved by using the empirical nonlocal pseudopotential of Stark and Falicov [10] to analyze the electron spectrum of cadmium. Simultaneously, we give a number of new experimental NMR results for the alloys Cd–Mg and Cd–Hg and demonstrate the possibility of using the Knight shift to investigate details of the band structure of disordered solid solutions.

Experimental Method and Results

NMR investigations of the alloys Cd–Mg and Cd–Hg were made in the hexagonal \( \alpha \) phase (with impurity concentration up to 12 at.%) and the body-centered tetragonal \( \omega \) phase for the system Cd–Hg [14]. The measurements were made with broad-line NMR spectrometers: the model RYa–2301 at low and room temperatures and Varian 4200V at high temperatures. When necessary, digital accumulation of the signals was used to measure the spectra.

The magnesium and mercury concentration in the alloys was measured by chemical
TABLE 1. Isotropic Component of the Knight Shift Tensor on Cd$^{113}$ Nuclei as a Function of the Impurity Concentration \( x \) (in at. %)

<table>
<thead>
<tr>
<th>Temperature, ( ^\circ \text{K} )</th>
<th>( K_{iso}(K_0+\Delta K \cdot x) \cdot % )</th>
</tr>
</thead>
<tbody>
<tr>
<td>20.4</td>
<td>( 0.348+0.006 \cdot x )</td>
</tr>
<tr>
<td>298</td>
<td>( 0.415+0.009 \cdot x )</td>
</tr>
<tr>
<td>298</td>
<td>( 0.550+0.0018 \cdot x )</td>
</tr>
<tr>
<td>298</td>
<td>( 0.593+0.0022 \cdot x )</td>
</tr>
</tbody>
</table>

Fig. 1. Concentration dependence of the component \( K_{iso} \) on Cd$^{113}$ nuclei for isovalent alloys of cadmium. The black circles and open circles correspond to \( T = 20.4^\circ \text{K} \) and \( T = 298^\circ \text{K} \); the crosses correspond to the liquid phase.

Discussion of the Results

A number of facts indicate that band effects are important in the Knight shift of isovalent cadmium alloys.

1. The temperature dependences of the components \( K_{iso} \) and \( K_{an} \) of the shift in pure cadmium are due [1, 2] to a rearrangement of the band structure that can be well described by the empirical nonlocal Stark–Falicov pseudopotential [10, 11]. Similar temperature dependences exist in the cadmium \( \alpha \) phase of the alloys Cd-Mg and Cd-Hg (Fig. 1 and [12, 15, 16]).

2. The concentration dependence of \( K_{iso} \) is correlated to the temperature dependence: both are less in the tetragonal \( \omega \) phase of the cadmium–mercury alloys and are completely absent in the liquid state (Fig. 1 and Table 1).

3. The Knight shift in the liquid phase, in which band-structure notions evidently cease to hold, corresponds to free electrons and is very different from the solid-state shift. The calculated free-electron value of \( K_{iso} \) (according to the data of [2]) is shown by the broken line in Fig. 1.

4. The behavior of the Knight shift tensor on the nuclei of the matrix (Cd$^{113}$, Cd$^{111}$) and the impurity (Hg$^{199}$) is exactly the same. In fact, for the \( \alpha \) phase of the alloys Cd-Hg the ratio \( A_{Hg}/A_{Cd} \) (where \( A = K_{an}/K_{iso} \)) for different temperatures and concentrations of the impurity is close to unity, and the mean value obtained from the data analysis and x-ray diffraction (using the change in the lattice parameters of the alloys [15]). All the measurements were made on polycrystalline powder samples.

The components \( K_{iso} \) and \( K_{an} \) of the Knight shift tensor were determined, as before [12, 15], by mathematical analysis of the shape of the resonance absorption lines.

Figure 1 shows the results of measurements of the isotropic part of the Knight shift on Cd$^{113}$ nuclei for the alloys Cd-Mg and Cd-Hg in the \( \alpha \) and \( \omega \) phases in the solid (at \( T = 20.4^\circ \text{K} \) and \( T = 298^\circ \text{K} \)) and liquid states. Each experimental point in Fig. 1 is the mean of 8 to 10 measurements. The continuous straight lines were found by the method of least squares. The slope corresponding to the increase of \( K_{iso} \) with the impurity concentration \( x \) is illustrated by Table 1.