

ever Burns and Wickner have pointed out that q is very sensitive to an internal cell structure parameter and that at a value quite close to the observed value, and within the experimental error of the X-ray experiments, q actually goes through zero. It seems possible therefore that the temperature dependence of the quadrupole effect is a consequence of a temperature dependence in this internal cell structure parameter.

JOURNAL OF THE PHYSICAL SOCIETY OF JAPAN

VOL. 17, SUPPLEMENT B-I, 1962

PROCEEDINGS OF INTERNATIONAL CONFERENCE ON MAGNETISM AND CRYSTALLOGRAPHY, 1961, VOL. I

Knight Shifts in the Intermetallic Compound PtSn_2 *

S. S. DHARMATTI, V. UDAYA SHANKAR RAO
AND R. VIJAYARAGHAVAN

*Tata Institute of Fundamental Research
Bombay, India*

Introduction

It has been found by Rowland¹⁾ that the Knight shift of Pt^{195} resonance in platinum metal is rather unusual in that it shows a large negative shift (-3.52%) with respect to its resonance in 1 molar chloroplatinic acid whereas normally in metals the shift is positive. Some light is thrown on its possible origin when one notes that a negative hyperfine interaction has been observed in the paramagnetic resonance spectra of Mn^{++} ion, which has a half-filled $3d$ electron shell with a net spin of $5/2$. The theory of Abragam and Pryce²⁾ to explain this, by a mechanism in which one of the $3s$ electrons is promoted to a higher s state, has not been very successful to account for the magnitude of the interaction, though qualitatively it explained the origin of the negative interaction. On the other hand, Heine³⁾, and Wood and Pratt⁴⁾ have independently shown that the negative hyperfine interaction arises as a result of the inner s -shell electrons becoming unpaired due to exchange interaction with the $3d$ electrons. This mechanism could quantitatively account for the observed interaction in Mn^{++} . Goodings and Heine⁵⁾ have shown that the above explanation can also account for the fact that the effective magnetic field at the iron nucleus is directed

oppositely to the electron magnetization. Therefore, in principle, there is no difficulty of understanding the occurrence of the negative Knight shift in platinum metal which has an unfilled $5d$ electron band. We wanted to study the effect of alloying on the Knight shift of Pt^{195} as there is a possibility of filling up of the d electron band with the electrons given by the guest metal, with which platinum is alloyed. A filling of the d electron band, would be expected to decrease its contribution to the magnetic susceptibility and thus give rise to a reduction in the exchange polarization. Hence the magnitude of the negative Knight shift should decrease or even assume a positive value. We studied the Pt^{195} and Sn^{119} resonances in the intermetallic compound PtSn_2 , having a cubic structure, isotypic with CaF_2 .

Experimental Results and Discussion

It is observed, that the Knight shift of Pt^{195} in PtSn_2 is -0.16% with respect to 1 molar chloroplatinic acid solution. Thus there is a large reduction in the magnitude of the negative Knight shift of this isotope from that of pure platinum metal. Pure platinum metal is paramagnetic with $\chi=1 \times 10^{-6}$ e.m.u./gm. A measurement of the susceptibility of the alloy showed that it has been reduced by a factor of four. This fall in the susceptibility is an indirect evidence

* Submitted for publication, in a condensed form, in "Il Nuovo Cimento".

for the conjecture that the d electron band in the alloy is nearly filled. The peak to peak line width of the absorption line is 2.1 g. The Knight shift, susceptibility and line width were all measured at room temperature.

The Knight shift of Sn^{119} in PtSn_2 is positive and is 1.06% in magnitude with respect to saturated SnCl_2 solution. This is the highest reported Knight shift so far for tin. The Knight shift⁽⁶⁾ in pure tin metal is +0.73% and it has been shown by Bloembergen and Rowland⁽⁶⁾ that the line is markedly asymmetric. White tin has a tetragonal structure and the asymmetry of the Sn^{119} resonance in the pure metal is ascribed⁽⁶⁾ to the absence of cubic symmetry. The resonance line of Sn^{119} in PtSn_2 is symmetric in the range of the magnetic field 2.5 to 5 kg as observed by us. This is consistent with the fact that, in PtSn_2 , tin is situated in a cubic environment. The peak to peak line width of the absorption curve is 3.8 g.

All the measurements were made on a wide line spectrometer of the Bloch type at room temperature. The alloy was made in the usual manner, by melting a mixture of pure platinum and tin in the appropriate proportion at 1100°C in an atmosphere of argon. The alloy was then powdered by filing and there was no difficulty in obtaining sample size less than the skin depth at the operating frequency. The powdered alloy was then annealed at 700°C for five days after which the X-ray powder pattern showed that the alloy was completely formed in the phase PtSn_2 . Before annealing, the alloy yielded two resonances for each of the isotopes Pt^{195} and Sn^{119} . The X-ray examination showed that part of the sample was in the hexagonal phase Pt_2Sn_3 . We could thus conclude that the two resonances obtained for each isotope were due to the two distinct phases PtSn_2 and Pt_2Sn_3 . The resonance lines, which disappeared on annealing, could therefore be attributed to the phase Pt_2Sn_3 . On this assumption, the Knight shift of Pt^{195} in Pt_2Sn_3 is -0.01% and that of Sn^{119} in Pt_2Sn_3 is +0.72%. It can be seen that, in the

Pt_2Sn_3 , the Pt^{195} resonance occurs near the Pt^{195} resonance in chloroplatinic acid, while the Sn^{119} resonance occurs near that of the tin metal. These measurements will be confirmed by making the observations on an alloy, completely in the phase Pt_2Sn_3 .

Conclusions

The larger negative Knight shift in pure platinum metal seems to be characteristic of the pure metal and has been attributed to the unfilled $5d$ electron band. When it is alloyed with a metal, the filling of the $5d$ electron band by the electrons of the guest metal reduces the magnitude of the Knight shift and moves the resonance towards the insulator point. It is interesting to compare the Knight shift of Pt^{195} in PtSn_2 with that in PtAl_2 , PtGa_2 and PtIn_2 , investigated by Jaccarino *et al.*⁽⁷⁾ In these alloys they found a positive Knight shift for Pt^{195} (with no values reported so far) while in PtSn_2 it shows a negative Knight shift although all the four alloys have identical cubic structure of the CaF_2 type.

It would be interesting to study the alloys, more rich in platinum than the above mentioned ones, in order to examine the effect of partially filling the $5d$ electron band on the Knight shift of Pt^{195} . It would be of further interest to study the temperature dependence of the Knight shift in the above alloys and to attempt a correlation with the temperature dependence of the magnetic susceptibility. Efforts in this direction are in progress.

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