Hyperfine interaction in ^{199}Hg$^+$ and ^{201}Hg$^+$ ($6s^1$): electron paramagnetic resonance studies of Hg$^+$ in NH$_4$Cl single crystals

Hyperfine interaction in ^{199}Hg$^+$ and ^{201}Hg$^+$ (6s^1): electron paramagnetic resonance studies of Hg$^+$ in NH$_4$Cl single crystals

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Abstract. The mercurous ion Hg$^+$ is produced by γ irradiation of Hg^{2+}-doped ammonium chloride single crystals, and electron paramagnetic resonance studies of it have been conducted in the 10–300 K temperature range. It is shown that Hg$^+$ occurs substitutionally at the NH$_4^+$ site. For odd isotopes of mercury, ^{199}Hg and ^{201}Hg, hitherto unreported transitions have been observed and are found to be highly sensitive to variations in the hyperfine coupling constant A, and thereby to the temperature dependence of A. The temperature dependence of A (for odd isotopic species) has shown an anomalous increase below the λ transition of ammonium chloride. The observation of new transitions has enabled the hyperfine coupling constants to be determined accurately and also the hyperfine anomaly for ^{199}Hg$^+$ and ^{201}Hg$^+$ to be re-estimated.

1. Introduction

Ammonium chloride has a simple-cubic structure at room temperature and it exists in different polymorphs in an easily accessible temperature range [1]. These features make it one of the most interesting lattices for investigations of the order–disorder behaviour of NH$_4^+$ and other related aspects of ammonium ion dynamics. It was one of the first systems in which ^{1}H NMR studies of ammonium dynamics in the solid state were carried out [2]. Subsequently, the effects of changes in ammonium ion dynamics on the g-value and hyperfine interactions of the Cu^{2+} dopant ion were studied by electron paramagnetic resonance (EPR) in this lattice [3, 4]. The simple-cubic structure was found to be extremely helpful in the stabilization of the divalent transition ions Cu^{2+}, Mn^{2+}, Ni^{2+} and Co^{2+} and also radiation-induced unusual valance states of Ni, Rh and Pd at interstitial sites [4–7]. Among the heavier elements, mercury is one of the most interesting for more than one reason. It is known that mercury can be stabilized as Hg$^+$ by ionizing radiation [8, 9]. This has the outer electronic configuration 6s^1 with a ^{2}S$_{1/2}$ ground state, which would make its EPR easily observable over a wide temperature range. The 's' character of the unpaired electron results in very strong hyperfine interaction for odd isotopes of mercury (mercury has six major stable isotopes with different nuclear spins, namely the even isotopes ^{198}Hg (10.02%), ^{200}Hg (23.13%), ^{202}Hg (29.8%) and ^{204}Hg (6.85%) with nuclear spin $I = 0$ and the old isotopes ^{119}Hg (16.84%) and ^{201}Hg (13.2%) with $I = \frac{1}{2}$ and $\frac{3}{2}$, respectively). Therefore, the Hg$^+$ ion in a lattice such as ammonium chloride is ideally suitable for detailed experimental investigation of various aspects such as the stabilization of unusual Hg$^+$ in a highly symmetric environment and the effects of the order–disorder transition on the hyperfine couplings in monovalent ^{199}Hg and ^{201}Hg which are among the strongest that can be encountered in EPR. Further, the large hyperfine coupling helps in the possible detection

of 'volume effects' in the hyperfine interaction when hyperfine structure (HFS) due to more than one isotope is observed. EPR investigations of Hg^+ ions have been reported earlier for various matrices such as $HClO_4$, CH_3CH_2OH, Cd acetate, $K_2M(CN)_4$ where $M = Zn$, Hg and Cd, potassium dihydrogen phosphate (KDP), ammonium dihydrogen phosphate (ADP) and $Hg(NO_3)_2$ [8–14]. In the present paper, EPR investigations of Hg^+ centres produced by γ irradiation of ammonium chloride single crystals doped with Hg^{2+} are reported. In contrast with the work reported earlier wherein the HFS information was obtained from a single EPR line for each of the odd isotopes, we report, for the first time, additional transitions at high fields for ^{199}Hg and ^{201}Hg which have been found to be highly sensitive to variation in temperature and have given more precise fitting for A'- and g-values. This identification has enabled the hyperfine coupling constants to be evaluated more precisely than those that could be obtained with a single $\Delta m_F = \pm 1$ transition. This allowed us to estimate the hyperstructure anomaly for $^{199}Hg^+$ and $^{201}Hg^+$ ions.

2. Experimental details

Ammonium chloride crystals were grown by slow evaporation of its neutral water solution containing 2% $HgCl_2$ and 10% urea by weight. Urea has been added to suppress the dendritic growth of the crystal [4] and it does not enter the lattice. The crystals were of good quality with well developed (100) planes and were almost colourless. The EPR spectra were recorded on a Bruker ESP-300 X-band (9.50–9.75 GHz) spectrometer. The crystals were γ irradiated at room temperature using a ^{60}Co source of up to 300 kGy. EPR investigations were carried out in the temperature range 10–300 K using a closed-cycle helium refrigerator obtained from M/s APD cryogenics with a Lakeshore temperature controller having an accuracy of better than ± 1 K.

3. Results and discussion

3.1. Identification of Hg centres

Ammonium chloride crystals doped with Hg^{2+} did not show any EPR signal down to 77 K. In samples γ irradiated at room temperature, EPR lines showing a strong temperature dependence of both intensity and line position were observed. These consist of an intense line at around $g \simeq 1.9995$, other lines due to radiation-induced intrinsic defects at around $g \simeq 2$, and more interestingly four additional lines at fields greater than 5 kG and extending up to 13.5 kG, the highest field that could be attained using our magnet. The positions of these lines (labelled B, C, D and E in figure 1) are 5.646 kG, 7.347 kG, 12.337 kG and 12.823 kG, respectively, at 10 K.

The dopant ion Hg^{2+} is diamagnetic and, on γ irradiation, Hg^{2+} can trap either an electron to form Hg^+ or a hole to form Hg^{3+}, and both centres will be paramagnetic. The cumulative abundance of even isotopes with $I = 0$ adds up to 70% and the EPR spectrum arising from them will not show any HFS. The intense line at $g = 1.997$ (at 10 K) is assigned to the even isotopic species of the paramagnetic Hg ion. The closeness of its g-value to the free-electron value clearly suggests that the paramagnetic Hg ion is monovalent Hg^+ with the electronic configuration $5p^6 5d^{10} 6s^1$. This is consistent with a number of earlier reports on the radiation stabilization of Hg^+ in various matrices [8–14]. Further the spectrum does not consist of simple $2I + 1$ doublet or a quartet because of hyperfine interaction with $I = \frac{1}{2}$ or $\frac{3}{2}$, respectively, and no EPR lines were observed at low fields. It is also similar to
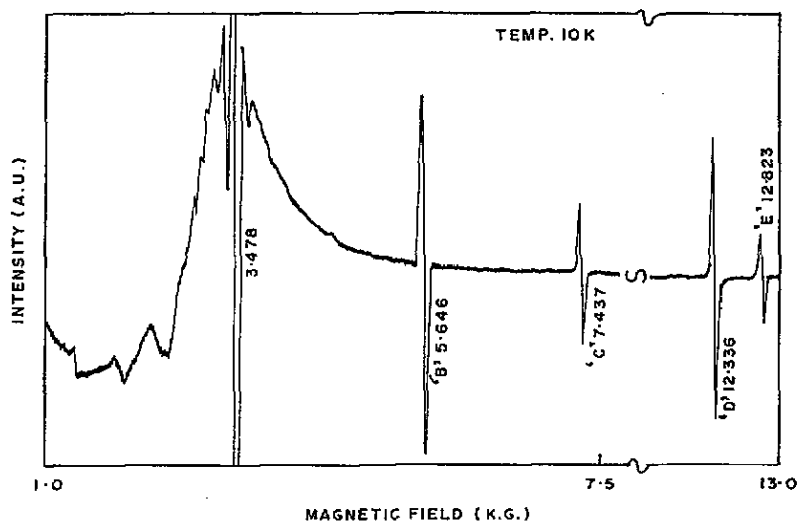
Figure 1. The EPR spectrum of a γ-irradiated Hg:NH$_4$Cl single crystal at 10 K with the magnetic field parallel to the (100) axis (A.U., arbitrary units).

what has been reported earlier for Hg$^+$ in different lattices. This suggests that the hyperfine coupling constant $A \gg h\nu$ for both ^{199}Hg$^+$ and ^{201}Hg$^+$ and the large value of A gives rise to the high-field lines shown in figure 1.

The EPR spectrum of monovalent mercury in ammonium chloride was found to be angle independent, both at room temperature and at 77 K in crystallographic (100) and (110) planes, establishing the isotropic nature of the spectrum. It is assumed that the spectrum remains isotropic down to 10 K. The earlier work on divalent transition-metal dopants in ammonium chloride has shown that they enter the lattice at interstitial sites with local D$_{4h}$ symmetry [4–7]. The interstitial position in these cases could be established by the 13-line chlorine superhyperfine structure (SHFS). The absence of such SHFS, in addition to the isotropic nature of the spectrum suggests that Hg$^+$ has entered at a substitutional NH$_4^+$ site experiencing a cubic symmetry. It may be noted that all divalent transition-metal ions have ionic radii ranging from 0.6 to 0.7 Å, whereas Hg^{2+} and NH$_4^+$ have much larger ionic radii in the range 1.2–1.43 Å [15]. Therefore it is inferred that Hg$^+$ is stabilized at the cation site in the ammonium chloride lattice. EPR spectra were recorded in the region 5.0–12.5 kG at different temperatures from 10 to 300 K. It was observed that the lines at around 5.646 kG (B) and 7.347 kG (C) were very weakly temperature dependent while high-field lines above 10 kG (D and E) show very strong temperature dependences. In particular, line D was found to shift clearly towards a higher field whereas line E shifted towards lower fields on increase in the temperature.

3.2. *Identification of the spectra*

The lines at around 5.646 kG (B) and 7.347 kG (C) agree with those reported by earlier workers for Hg$^+$ ions due to hyperfine coupling with $I = \frac{1}{2}$ and $I = \frac{3}{2}$ for ^{199}Hg and ^{201}Hg, respectively [8–14]. Lines D and E observed at much higher fields, i.e. 12.332 kG and 12.823 kG (10 K), have not been reported in any other lattice. The intensities of these lines exhibited temperature dependences similar to those of lines B and C. In the next section
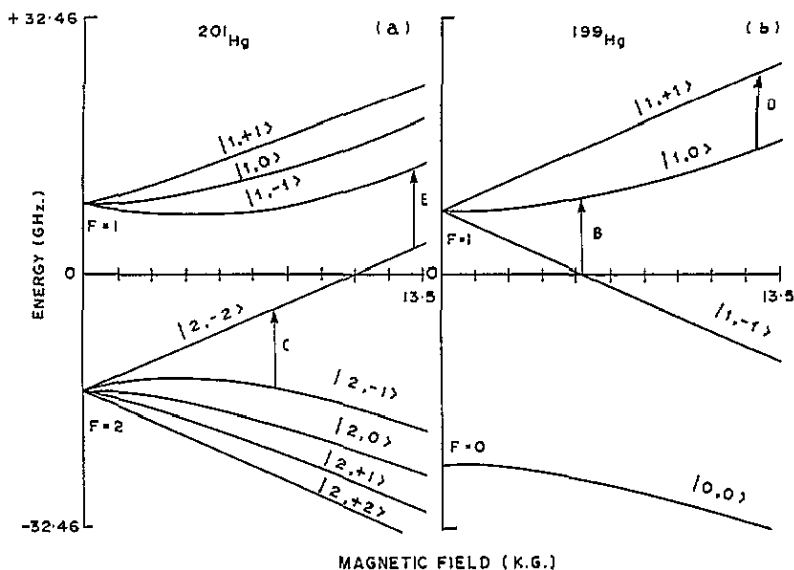
Figure 2. Energy level diagram for the total angular momentum quantum number F (a) for ^{201}Hg$^+$ and (b) for ^{199}Hg$^+$ as a function of magnetic field.

it is shown that these belong to hitherto unreported $\Delta m_F = \pm 1$ transitions belonging to ^{199}Hg$^+$ and ^{201}Hg$^+$ species, respectively.

3.3. Calculation of the hyperfine coupling constants

The EPR spectrum as discussed above is identified as being due to the Hg$^+$ ion in cubic symmetry. This is a case of a hydrogen-line configuration with a $^2S_{1/2}$ ground state, but with very large hyperfine coupling. The coupling between electron and nuclear spins of odd isotopic species gives rise to the total angular momentum $F = I + S$ with the coupling constant A. In the case when A is much larger than the electronic Zeeman term (typically of the order of 0.3 cm^{-1}), the external magnetic field cannot decouple the nuclear and electronic spins and the EPR spectrum arises owing to $\Delta m_F = \pm 1$ transitions. Such cases have been worked out elegantly by Breit and Rabi [16]. The energy as a function of F and m_F is given by

$$E(F, m_F) = -\frac{\Delta W}{2(2I + 1)} + g_N \beta_N H m_F \pm [1 + 4m_F X/(2I + 1) + X^2]^{1/2} \Delta W/2 \qquad (1)$$

where $\Delta W = [(2I + 1)/2]A$ and $X = (g\beta - g_N\beta_N)H/\Delta W$. Under zero-field conditions, the energy levels of ^{199}Hg$^+$ for $F = 1$ and $F = 0$ are separated by ^{199}A and in the case of ^{201}Hg$^+$ energy levels for $F = 1$ and $F = 2$ are separated by $2^{201}A$. For calculation of the energy levels, the g-value from the even isotope is used and A has been varied between 25 and 35 GHz for ^{199}Hg$^+$ and between 10 and 15 GHz for ^{201}Hg$^+$ so as to attain suitable fitting with the experimental data.

Figures 2(a) and 2(b) show the energy level diagrams for the m_F-values as a function of the magnetic field for ^{201}Hg and ^{199}Hg, respectively, in their monovalent forms. In calculating these energy levels the best-fit field values of the hyperfine parameters at 10 K were used. The allowed transitions ($\Delta m_F \pm 1$) that can be observed at a microwave frequency of 9.74 GHz are labelled in figure 2 as B, C, D and E.

The dependence of resonance fields on the value of A was investigated using equation (1). It was observed that the positions of lines B and C are relatively less sensitive to the changes in the value of A in contrast with the high-field lines D and E. Typically a change in ^{199}A by 100 MHz resulted in a shift in the position of line B by 2.5 G and that of line D by 43 G. Similarly a change in ^{201}A by 45 MHz resulted in shifts in the positions of lines C and E by 9.3 G and 157.5 G, respectively. From this it is observed that $(dH/dA)^{-1}$ for transitions D and E are 2.5 MHz G^{-1} and 0.25 MHz G^{-1}, respectively. The difference between the calculated and observed field values for lines D and E are 2 G and 5 G, respectively. This shows that the error in ^{199}A is 5 MHz and the error in ^{201}A is 1.25 MHz. It may be noted these values refer to data at 10 and 70 K where the high-field lines are intense enough for accurate measurement of field values. Thus the strong dependence of the positions of lines D and E on A-value enabled reasonably accurate determination of A for these isotopes to be made. The g- and A-values for Hg^+ in different lattices are summarized in table 1. It can be seen that the ^{199}A and ^{201}A obtained for NH_4Cl are among the highest reported for Hg^+ in the solid state.

Table 1. g- and A-values for Hg^+ in different lattices.

Lattice	g	^{199}A	^{201}A	Reference
7 M $HClO_4$ (77 K)	1.997	12 000		[8]
CH_3CH_2OH (77 K)	1.987	11 500		[8]
$Hg(CH_3CO_2)_2$ (300 K)	1.999	9007		[9]
$Cd(CH_3CO_2)_2$ (300 K)	1.984	9100		[9]
$Cd(CH_3CO_2)_2$ (300 K)	1.9967	29 205	−10 791	[10]
KDP (300 K)	1.9965	34 557		[14]
ADP (300 K)	1.9959	33 959		[14]
$Hg(NO_3)_2$ (77 K)	1.994	35 300	−12 900	
$Hg:NH_4Cl$ (10 K)	1.9995	32 060	−11 875	Present work
$Hg:NH_4Cl$ (70 K)	1.9985	31 800	−11 810	Present work
$Hg:NH_4Cl$ (300 K)	1.9910	29 900	−11 050	Present work

3.4. Temperature dependence of A

The temperature dependence of A is shown in figure 3. This shows a sharp increase in A, below the λ transition (243 K) where NH_4^+ ions go into an ordered state [1]. The values of the hyperfine constants have been reduced by 26% at 300 K and by 21% at 10 K with reference to their free-ion values (the free-ion values reported [14] for ^{199}A and ^{201}A are 40.507 GHz and 14.995 GHz, respectively). This change reflects the change in degree of covalency of the Hg–Cl bond in the NH_4Cl lattice at the λ transition if no other factors are taken into account in the temperature dependence of A. It is interesting to note that the degree of s-electron delocalization decreased in the low-temperature phase despite a sudden volume contraction at the λ transition. The temperature dependence of the hyperfine coupling constant A for S-state ions in different matrices has been reported by Walsh *et al* [17], Orbach and co-workers [18–20] and more recently Shrivastava [21]. These workers suggest that the phonon-induced configuration mixing appears to play an important role in the temperature dependence of A. The most striking feature in the present study is the sudden change in A at the λ transition. It is well known that this phase transition is associated with the orientational order–disorder of NH_4^+ ions. In the disordered state the effective symmetry at the Hg^+ site can be much less than cubic if the orientation of NH_4^+

is taken into account. Kuroda and Kawamori [22] explained the temperature dependence of spin-Hamiltonian parameters g and A of Cu^{2+} in NH_4Cl by considering the admixtures of electronic states brought about by the disordered orientation of NH_3 groups bonded to the Cu^{2+} ion. Kuroda and Kawamori [22] have also shown that the temperature dependence of A for Cu^{2+} followed the temperature dependence of the order parameter of NH_4^+ ions in pure ammonium chloride obtained by the numerical integration of the specific heat. Therefore the order-disorder of ammonium ions has an effect similar to the phonon-induced temperature dependence of A for many S-state ions, particularly in the temperature range above 150 K. The temperature dependence of A is expected to arise owing to motional averaging between different possible orientations of six first-neighbour ammonium ions. The probability that all six neighbours are simultaneously in either of the two possible positions, in the disordered phase, is $2 \times (\frac{1}{2})^6 = \frac{1}{32}$ and hence the probability that the Hg^+ ion experiences a disordered NH_4^+ neighbourhood is $\frac{31}{32}$. The temperature dependence of A essentially reflects the temperature dependence of the orientational order parameter of NH_4^+, which goes from $\frac{1}{32}$ to 1 across the phase transition. This suggests that the correlation time characterizing this process is shorter than the inverse of the difference between A for the ordered and disordered states. This is of the order of $(0.6 \times 10^9)^{-1} = 1.6 \times 10^{-7}$ s. This is an order of magnitude smaller than the reported correlation time of NH_4^+ reorientation, 1.6×10^{-6} s [22]. The shorter time scale in the present case represents the correlation among the six first-neighbour cations around the Hg^+ site.
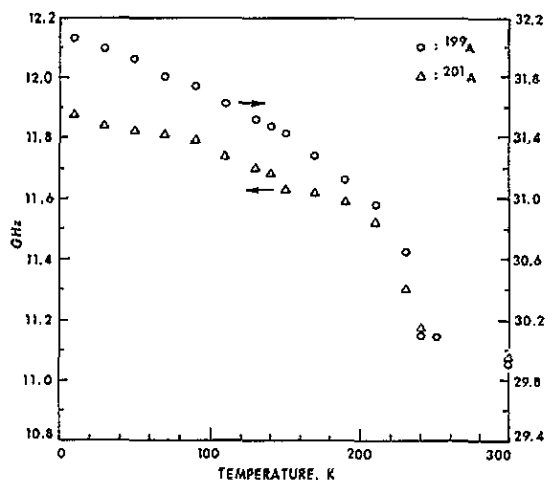

Figure 3. Temperature dependence of the hyperfine coupling constant A for $^{201}Hg^+$ and $^{199}Hg^+$ in the ammonium chloride lattice.

The order parameter of ammonium ions attains the value of unity below 150 K [22] and, therefore, the temperature dependence of A between 10 and 150 K arises only because of phonon-induced configurational mixing as suggested by Walsh *et al* [17]. This is also apparent in the differences between the temperature dependences of ^{199}A and ^{201}A, as can be seen in figure 3. The hyperfine coupling of the lighter isotope (^{199}Hg) is more strongly temperature dependent than that of the heavier isotope. The discussion on the hyperfine coupling constants and their temperature dependence may be summed up by stating the following: the hyperfine coupling constants at 10 K are less than the respective free-ion

values by 20%, which gives the degree of covalency of the Hg–Cl bond. The coupling constants are further reduced by 2.7% owing to vibrational admixtures of the electronic states in the 10–150 K temperature range and another 4% because of orientational disorder of ammonium ions as the sample was cooled through the λ transition.

3.5. The hyperfine anomaly

In the case of the isotropic hyperfine interaction, s electrons play the most important role because of their penetration into the nuclear volume. In a normal case, where no relativistic effects are important, the ratio of hyperfine coupling constants of two isotopic species will be in the ratio of their respective nuclear magnetic moments [23]. However, for heavy elements, when the relativistic effects become important, a hyperfine anomaly Δ arises and is defined as

$$A_1/A_2 = \Gamma_1/\Gamma_2(1 + \Delta)$$

where A_1 and A_2 are the isotropic hyperfine coupling constants of two different isotopes, and Γ_1 and Γ_2 are the respective nuclear gyromagnetic ratios. For ^{199}Hg$^+$ and ^{201}Hg$^+$, the hyperfine anomaly was earlier reported by Dalal *et al* [10] to be 0.16%. In view of the fact that the additional hyperfine interaction data obtained in the present study gave more precise values of A, we have re-estimated the hyperfine anomaly Δ. It can be seen that $^{199}A/^{201}A = 2.7$ at 10 K and 2.693 at 70 K. The value of the ratio of gyromagnetic ratios [24] is $^{199}\Gamma_N/^{201}\Gamma_N = 2.709\,008$.

The values of Δ were found to be -0.0034 at 10 K and -0.006 at 70 K. The percentage error in the $^{199}A/^{201}A$ was estimated to be of the order of 0.4%. Therefore the absolute value of Δ varies from 0.006 ± 0.004 at 70 K to 0.0034 ± 0.004 at 10 K. The hyperfine anomaly is not expected to be temperature dependent and hence these values may be taken as an indication of the possible spread in the experimental values of Δ. Grandinetti *et al* [13] have reported a temperature-dependent Δ for monovalent mercury in the ADP lattice from which they inferred that nuclear shapes were affected in antiferroelectric ADP by dielectric polarization. As the quadrupole moment of a nucleus depends only on the nuclear shell structure, it is most unlikely that it is affected by extrinsic factors such as dielectric polarization. However, there is one possible case where the hyperfine anomaly would be temperature dependent [25]. These are the cases of molecular radicals in which the different vibrational behaviours of isotopically different species dominate all other factors contributing to the temperature dependence of A. If there is a significant contribution of electron–phonon interaction to the temperature dependence of A, it can be argued that it gives rise to a temperature-dependent Δ. As discussed earlier in the low-temperature ordered phase of ammonium chloride, the different extents of temperature dependences in ^{199}A and ^{201}A arise becuse of the different extents of electron–phonon contributions to the respective isotopic species. In view of this, greater weightage may be given to the value of Δ at 10 K rather than to that at 70 K. This gives a percentage value for the hyperfine anomaly of about 0.34%, which is significantly more than the 0.16% reported earlier [10]. In view of the absence of quadrupole interaction in the present case and also the availability of experimental data sensitive to variations in A, we believe that Δ is of the order of 0.34%.

4. Conclusion

In conclusion, the present work provides clear evidence about the Hg$^+$ ion entering substitutionally at the NH$_4^+$ site in the NH$_4$Cl matrix. The two additional transitions observed

above 10 kG have been identified as $|F = 2, m_F = 0\rangle$ to $|F = 1, m_F = 1\rangle$ for ^{199}Hg and $|F = 2, m_F = -2\rangle$ to $|F = 1, m_F = -1\rangle$ for ^{201}Hg ions. These studies have also enabled the hyperfine constants for ^{199}Hg and ^{201}Hg to be determined precisely, leading to re-estimation of the hyperfine anomaly.

Acknowledgment

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