A Mössbauer Effect Study of a Phase Transition in $^{57}Fe^{2+}$ Doped Ammonium Chloride

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The lambda transition in ammonium chloride at 242 K has been investigated using $^{57}Fe^{2+}$ impurity atoms. These probably reside on interstitial sites in an effective $[FeCl_4(H_2O)_2]^{2-}$ complex. The temperature dependence of the quadrupole splitting reveals a larger tetragonal distortion of the impurity site in the low-temperature ordered state of the NH_4Cl.

AMMONIUM chloride undergoes a lambda-transition of the order–disorder type at 242 K which involves the relative orientation of the tetrahedral ammonium ions at the body centre of the CsCl-type lattice.[1] In the low-temperature ordered state, all the NH_4^+ tetrahedra have the same orientation with respect to the crystallographic axes (at least for a given domain). In the high-temperature disordered state they are randomized between the two possible equivalent orientations. Thermal expansion data reveal an anomalous discontinuous lattice expansion (0·3% increase in the lattice parameter) as one goes from the ordered to the disordered state, together with a hysteresis of 0·21 K.[2] The latter feature is confirmed by the specific heat data.[3] For reasons as yet unexplained, the magnitude of the specific heat anomaly is strongly dependent on the individual sample. Both the thermal expansion [2] and ultrasonic measurements [4] confirm that the transition is not of a simple lambda-type, but because of an instability in the immediate vicinity of the critical point is found experimentally at atmospheric pressure to be a first-order transition.

In the present work we have investigated the transition using the ^{57}Fe Mössbauer resonance in ammonium chloride crystals containing enriched $^{57}Fe^{2+}$ impurity ions. The sensitivity of the resonant atom to its crystalline environment provides a means of studying temperature dependent changes in the latter. A second phase transition in ammonium chloride from a CsCl- to a NaCl-type lattice at 456 K [1] was not investigated in the present work.

EXPERIMENTAL

Single crystals of ammonium chloride doped with ^{57}Fe were grown by slow evaporation of an aqueous solution containing less than one mole percent of $FeCl_2$ (enriched to 90% in ^{57}Fe). The cubic habit of the crystals was stimulated by including 10 wt. % of urea in the growth solution. The actual concentration of ^{57}Fe in the ammonium chloride was not determined.

Mössbauer spectra were recorded for oriented single-crystal matrices at room temperature, and for a powdered random-orientation sample in the range 118—293 K. The spectrometer embodied an MVT3 transducer, an MD3 drive amplifier, and an MFG3 waveform generator from Elscint Ltd., of Israel. These units were coupled with a Northern Scientific Inc. NS630 multichannel analyser. Low temperature measurements were made using a Ricor MCH5 variable temperature cryostat with a Ricor TC4B temperature controller. Temperature control, as monitored by the gold (0·03% Fe)–chromel thermocouple, was better than 0·1 K. The radioactive source was ^{57}Co in a palladium matrix. All spectra were analysed by computer fitting with two Lorentzian line profiles, and calibrated using the spectrum of an iron foil at room temperature.

Some preliminary data at temperatures below 118 K and above 293 K were obtained from the P.C.M.U. service

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[1] H. A. Levy and S. W. Peterson, *Phys. Rev.*, 1952, **86**, 766.

[2] G. E. Fredericks, *Phys. Rev. B*, 1971, **4**, 911.

[3] P. Schwartz, *Phys. Rev. B*, 1971, **4**, 920.

[4] C. W. Garland and R. Renard, *J. Chem. Phys.*, 1966, **44**, 1120, 1130.

(Harwell), and were not repeated in our own more detailed measurements.

RESULTS AND DISCUSSION

The Nature of the Impurity Site.—A prerequisite in any study of the phase transition is a knowledge of the lattice position occupied by the impurity atom. Evidence in this respect for the ammonium chloride doped with iron was obtained from oriented absorbers. The doped crystals can be grown as plates on the [100] plane, and are easily formed into a composite matrix with dimensions suitable for Mössbauer measurements. Such a matrix was used, initially aligned with the γ-ray beam parallel to a $\langle 100\rangle$ axis, so that it could be rotated about a $\langle 001\rangle$ axis. Spectra were obtained as the γ-ray beam was rotated by suitable increments from the $\langle 100\rangle$ axis towards the $\langle 110\rangle$ axis.

Each spectrum consisted of a resolved quadrupole doublet with narrow line widths, the chemical isomer shift ($\delta = 1{\cdot}18$ mm s^{-1} relative to Fe metal) and quadrupole splitting ($\Delta = 1{\cdot}97$ mm s^{-1}) being typical of a high-spin Fe^{2+} ion in octahedral co-ordination.[5] The relative intensities of the two components of the doublet proved to be angular-independent within experimental error.

The latter feature was unexpected, as such a single-crystal spectrum is usually angular-dependent in a way determined by the relationship of the electric field gradient tensor of the absorbing atom with respect to the crystallographic axes.[6] Although the NH_4Cl crystal as a whole has cubic symmetry, that of the iron impurity site can be inferred to be tetragonal or lower from the presence of the quadrupole splitting. However, in the event that the impurity sites are all equivalent, and also that they feature a principal axis pointing in one of three mutually orthogonal directions such as the $\langle 100\rangle$, $\langle 010\rangle$, and $\langle 001\rangle$ axes with equal probability, then it is easily shown (see Appendix) that the observed Mössbauer spectrum will be angular-independent in a single crystal. Furthermore, the comparatively large value for the quadrupole splitting would favour a $|d_{xy}\rangle$ singlet ground state. Some incomplete e.s.r. studies of Fe^{2+}-doped NH_4Cl are consistent with a tetragonal site symmetry,[7] but otherwise do not throw any further light on the possible nature of the iron(II) complex.

There are two possible positions of the Fe^{2+} ion in NH_4Cl which are consistent with the experimental data. The first of these is a substitutional Fe^{2+} ion at an NH_4^+ site, associated with a nearest-neighbour cation vacancy. It is not easy to assess the effect on the Mössbauer parameters of the eight-fold co-ordination to chlorine because of lack of comparative data.

The alternative is an interstitial position for the Fe^{2+} ion at a face-centre of the chloride ion cube, associated with a pair of NH_4^+ vacancies to preserve charge neutrality. Evidence in favour of this possibility comes from e.s.r. and electronic absorption studies of other divalent transition metals in NH_4Cl. It is usually found that the cation vacancy sites are occupied by a neutral molecule such as H_2O. Measurements on the Mn^{2+}-doped NH_4Cl are consistent with interstitial manganese in an effective tetragonal $[MnCl_4(H_2O)_2]^{2-}$ complex,[8,9] and similar substitution occurs with nickel,[10] and with copper.[11,12] Crystals grown from ammoniacal solutions have been found to contain the $[CuCl_4(NH_3)_2]^{2-}$ complex,[13] but in the present investigation Fe^{2+} impurity could not be stabilized in alkaline solutions and in all such attempted preparations it was oxidized to Fe^{3+}. Evidence was found in a number of our other crystal preparations for a small proportion of Fe^{3+} ion, but this was always small ($<5\%$ of total iron) and did not affect the main observations.

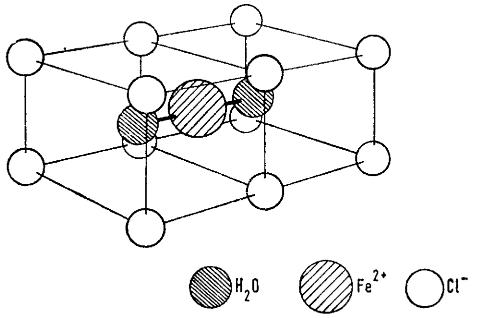

FIGURE 1 The postulated complex in Fe^{2+}–NH_4Cl

The use of urea to stimulate crystal growth does not appear to result in its incorporation in the crystal. In the only case where this has been detected (Cu^{2+}–NH_4Cl grown from a solution containing 25 wt. % urea) the concentrations in the solid were small (0·2 wt. %) and did not influence the impurity complex.[14]

An attempt was made to confirm the presence of an $[FeCl_4(H_2O)_2]^{2-}$ complex by growing crystals with a much higher concentration of natural iron and analysing for iron and water. Unfortunately, these results were inconclusive because several samples of the undoped NH_4Cl also contained a substantial but variable proportion of water. One can state, however, that the crystals contained sufficient water to form the postulated complex.

In summary, the Mössbauer and other less direct evidence are all consistent with the presence of an interstitial Fe^{2+} ion in a site of tetragonal symmetry, probably co-ordinated to water as illustrated in Figure 1, and with a d_{xy} ground state. This complex is similar in

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[5] N. N. Greenwood and T. C. Gibb, ' Mössbauer Spectroscopy,' Chapman and Hall, London, 1971.

[6] P. Zory, *Phys. Rev.*, 1965, **140**, A1401.

[7] M. M. Zaripov and G. K. Chirkin, *Soviet Phys. Solid State*, 1965, **7**, 74.

[8] D. H. Goode, *J. Chem. Phys.*, 1966, **45**, 1366.

[9] T. J. Seed, *J. Chem. Phys.*, 1964, **41**, 1486.

[10] P. A. Narayana and P. Venkateswarlu, *J. Chem. Phys.*, 1970, **52**, 5159.

[11] J. R. Pilbrow and J. M. Spaeth, *Phys. Stat. Sol.*, 1967, **20**, 225, 237.

[12] B. Bechtle, F. Boettcher, and J. M. Spaeth, *Phys. Stat. Sol.*, 1971, **43**, K169.

[13] N. Kuroda and A. Kawamori, *J. Phys. Chem. Solids*, 1971, **32**, 1233.

[14] S. H. Hagen and N. J. Trappeniers, *Physica*, 1970, **47**, 165.

many ways to the *trans*-octahedral structure of $FeCl_2,2H_2O$, and it is perhaps significant that the quadrupole splitting for this compound[15] at 77 K ($\Delta = 2{\cdot}63$ mm s^{-1}) is very similar to that of the Fe^{2+}–NH_4Cl complex at the same temperature ($\Delta = 2{\cdot}627 \pm 0{\cdot}002$ mm s^{-1}).

The NH_4Cl *Phase Transition.*—Mössbauer spectra were obtained from a polycrystalline Fe^{2+}–NH_4Cl matrix. The temperature dependence of the quadrupole splitting and chemical isomer shift between 144 and 296 K are illustrated in Figure 2. Because of the necessity of periodically recharging the refrigerant tank, the data were not all collected in the same series of measurements. They were also obtained in a semi-random sequence of temperature changes, but as will be seen they are fully self-consistent. However, because of experimental limitations it was not possible to produce such a complete set of consistent intensity and half-width data. For this reason we do not quote recoil-free fraction data. Nevertheless, it can be stated that the spectrum area decreased regularly by 26% between 194 and 273 K, without discontinuity at the lambda point, and that there was no significant intrinsic line broadening from an average observed value of 0·26 mm s^{-1} throughout this temperature range.

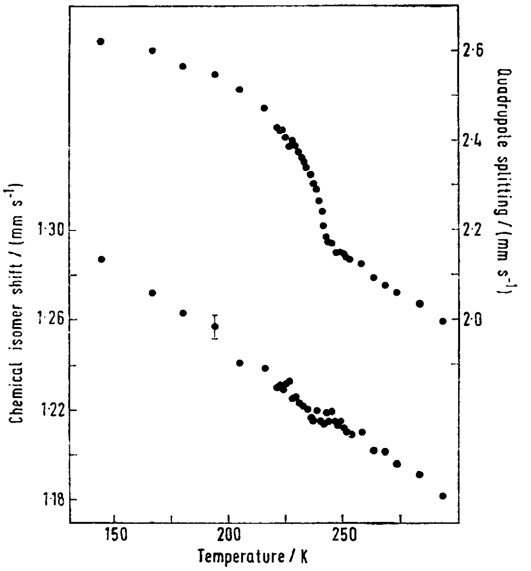

FIGURE 2 The temperature dependence of the quadrupole splitting and chemical isomer shift in Fe^{2+} doped NH_4Cl

The chemical isomer shift shows no discontinuity at the lambda point to within the observational accuracy of $\pm 0{\cdot}003$ mm s^{-1}. The temperature dependence of the chemical isomer shift is predominantly due to the second-order Doppler shift expressed as $\delta = \delta_0 - \langle v^2 \rangle / 2c$ where δ_0 is the shift that would exist in the absence of lattice vibrations, $\langle v^2 \rangle$ is the mean square velocity of the vibrating resonant nucleus, and c is the velocity of light. Although this aspect of the data was ancillary to our main objectives, we have carried out an analysis assuming an Einstein model for the iron impurity site following the approach of Johnson and Dash.[16] A least-squares fit to the data gave $\delta_0 = 1{\cdot}4$ mm s^{-1} and an Einstein temperature of 158 K.

The quadrupole splitting decreases markedly over an interval of 40 K below a temperature of 243 ± 1 K, *i.e.* the known phase transition in 'pure' ammonium chloride. This behaviour is unexpected as one might have expected that the discontinuous change in the lattice parameter at the phase transition would cause a discontinuity in the behaviour of the impurity site: in fact we see a substantial change taking place in the temperature region below the transition which ceases abruptly at the lambda point. However, the properties of the lattice in the immediate vicinity of the impurity may be controlled far more by this impurity than by the order–disorder process.

The temperature dependence of the quadrupole splitting of Fe^{2+} in an octahedral environment has been well studied.[17–20] The behaviour observed is determined largely by a combination of the tetragonal distortion and spin–orbit coupling, and can be used to determine the t_{2g} splitting.

The quadrupole splitting at any temperature T can be represented by[17,18] $\Delta = \Delta_0 F(\xi,\lambda,T)$ where $\Delta_0 = \frac{4}{7}\langle r^{-3} \rangle (1 - R)(e^2Q/2)$ is the quadrupole splitting appropriate to a single unpaired $3d$-electron in a $|d_{xy}\rangle$ ground state, and $F(\xi,\lambda,T)$ is a temperature-dependent factor less than unity which allows for thermal population of the $|d_{xz}\rangle$ and $|d_{yz}\rangle$ excited levels. These are assumed in this case to be degenerate (*i.e.* tetragonal symmetry) at an energy ξ above the ground state; λ is the spin–orbit coupling parameter, R is the Sternheimer shielding factor, Q is the nuclear quadrupole moment, e is the charge on the proton, and $\langle r^{-3} \rangle$ is the radial expectation value of the electron density.

This expression is in fact an approximation in that it ignores smaller contributions from lattice charges. The latter are often less sensitive to temperature but in this particular case, where there is a substantial change in lattice parameters, this may not be so. Calculations to interpret our data in terms of ligand-field parameters have been made using the methods described in an earlier paper.[18]

The quadrupole splitting data 4·2—356 K are shown in Figure 3. They may be considered in terms of three distinct regions, the first of which is the disordered phase above 243 K in which the quadrupole splitting shows considerable temperature dependence. The solid curve is a theoretical fit calculated using a spin–orbit coupling parameter of -80 cm^{-1} and neglecting the lattice terms. The relevant parameters are $\xi = 450$ cm^{-1} and $\Delta_0 = 3{\cdot}04$ mm s^{-1}. These should be regarded only as approximate values because of the uncertainty involved in fitting the data.

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[15] C. E. Johnson, *Proc. Phys. Soc.*, 1966, **88**, 943.
[16] D. P. Johnson and J. G. Dash, *Phys. Rev.*, 1968, **172**, 983.
[17] R. Ingalls, *Phys. Rev.*, 1964, **133**, A787.
[18] T. C. Gibb, *J. Chem. Soc.* (*A*), 1968, 1439.
[19] U. Ganiel and S. Shtrikman, *Phys. Rev.*, 1969, **177**, 503.
[20] D. P. Johnson and R. Ingalls, *Phys. Rev. B.*, 1970, **1**, 1013.

The temperature region below 200 K does not feature a substantial temperature dependence, contrasting with the theoretical prediction for a level separation of 450 cm^{-1} for example. This implies an effectively larger ligand field splitting such that ξ/λ is greater than in the disordered state. The two curves drawn were calculated for $\xi = 600\ \text{cm}^{-1}$, $\Delta_0 = 2{\cdot}77\ \text{mm s}^{-1}$ and $\xi = 900\ \text{cm}^{-1}$, $\Delta_0 = 2{\cdot}96\ \text{mm s}^{-1}$.

It is not possible to interpret the intermediate temperature region between 200—243 K because of lack of information.

Three observations which remain valid whether or not a lattice term is included in the calculations can be made. First, the ligand-field splitting is greater in the low-temperature ordered state and may be of the order of 900 cm^{-1} as compared to 450 cm^{-1} in the disordered state. This is fully consistent with the observed lattice expansion. However, in view of the observation [12] of a further distortion to orthorhombic symmetry in Cu^{2+} doped NH_4Cl below 20 K, we do not feel that a more detailed interpretation of the low-temperature data is justified at this juncture.

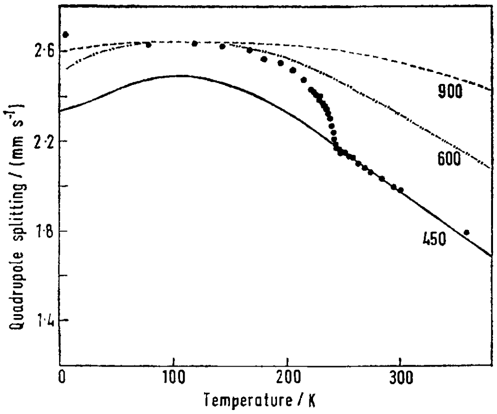

FIGURE 3 Theoretical analysis of the quadrupole splitting in terms of an axial splitting parameter. Curves for a t_{2g} splitting of 450, 600, and 900 cm^{-1} are shown

Second, the observed quadrupole splitting deviates markedly from prediction over a 45° interval below the lambda point, and seems to indicate that the effective ligand field parameter is changing continuously in this region. Similar substantial changes in the e.s.r. parameters of Cu^{2+}–NH_4Cl have been found below the lambda point over the same temperature range.[11,13] It was originally suggested that there is a substantial reduction in $\langle r^{-3}\rangle$ as the temperature is raised,[12] but a more recent paper has presented an alternative explanation for data on ammoniated crystals in which the order–disorder reorientation of the NH_3 molecules at the cation vacancies can generate the observed effects.[12] The present data do not contribute to this aspect of the discussion because it is not possible to determine $\langle r^{-3}\rangle$ independently.

The third observation is concerned more directly with the nature of the transition. The most recent thermal expansion and specific heat studies [2,3] on NH_4Cl show that the phase transition effects are seen only in the range 234—244 K. An interesting observation in the present study is that the Mössbauer spectrum shows substantial changes at much lower temperatures. However, the quadrupole splitting does change more rapidly between 234 and 244 K. There is a striking similarity between the temperature dependence of Δ and that of the hyperfine constant A in Cu^{2+}–NH_4Cl e.s.r. studies.[10,12] Both parameters reflect the nature of the electronic wave functions of the impurity atom, and would seem to suggest the onset above 190 K of a perturbation due to the tendency to disorder.

APPENDIX

The ratio of the areas under the two Mössbauer lines of an Fe^{2+} doublet, assuming isotropic recoilless absorption, is expressed in Zory's notation [6] as

$$\frac{A_3}{A_1} = \frac{\sum_i\{4[(3+\eta^2)/3]^{\frac{1}{2}} + (3\cos^2\theta_i - 1 + \eta\sin^2\theta_i\cos 2\phi_i)\}}{\sum_i\{4[(3+\eta^2)/3]^{\frac{1}{2}} - (3\cos^2\theta_i - 1 + \eta\sin^2\theta_i\cos 2\phi_i)\}}$$

The summation is over the number of equivalent sites. In the present case of Fe^{2+}–NH_4Cl there are three equivalent sites each with $\eta = 0$. When the crystals are rotated about the $\langle 001\rangle$ axis such that the γ-beam is in the [100] plane, the direction of the γ-beam will be perpendicular to the Z axis of one site and at angles of θ and $(90 - \theta)$ to the Z axes of the other two sites respectively. A simple substitution of these values in the above equation will show that $A_3/A_1 = 1{\cdot}0$ for all values of θ. This is a simple illustration of the angular independence of an Fe^{2+} quadrupole doublet if there are three equivalent sites with mutually orthogonal Z-axes. It can be easily shown that the spectrum also remains angular independent in all other crystallographic planes.

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