PARAMAGNETIC HYPERFINE INTERACTIONS OF IRON IN SOLID AMMONIA FROM MÖSSBAUER SPECTROSCOPY *

by

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ABSTRACT

Mössbauer studies on highly dilute ^{57}Fe in solid ammonia are reported. The hyperfine parameters of the paramagnetic reaction product FeNH$_3$ point to a nearly atomic configuration of iron [Ar]3d^{7}4s. The electronic spin relaxation slows down rapidly under application of an external magnetic field. The field dependence of the magnetic hyperfine patterns indicates a strong axial magnetic anisotropy.

Key-words: Mössbauer; Paramagnetic hyperfine interaction; Matrix
           isolation; Electronic spin relaxation; Criochemistry;
           Solid gas matrix.

1 INTRODUCTION

Mössbauer studies of the hyperfine interactions on atoms, small clusters and molecules isolated in inert frozen gases have been reported for various species[1,2]. Reaction products of atoms in frozen gases have been studied less often[1-4]. Small molecules formed in matrices are of interest for lowest temperature chemistry[5] and chemistry on surfaces[6]. In addition the combined information on electron densities, electric field gradients and magnetic hyperfine fields allow critical tests for first principle molecular orbital calculations of the hyperfine interactions in relatively small molecules. Mostly only the isomer shifts and quadrupole interactions were studied. The magnetic hyperfine interaction in isolated species could usually not be observed unless a magnetic field was applied since electronic relaxation is faster than nuclear Larmor precession. Mössbauer studies of the magnetic hyperfine interactions under applied external magnetic fields were reported for isolated atomic iron[7], iron dimers[8] and ionic states of iron[9].

We have studied the hyperfine interactions on the reaction product of atomic iron isolated in solid ammonia. The experiments were performed under applied external fields and at various temperatures. Previous matrix isolation studies on Fe in NH_3 and Fe in NH_3 mixed with Xe revealed the formation of a small molecule, presumably $FeNH_3$[3,4]. This was also supported by IR studies and UV photolysis[3]. From isomer shift and quadrupole interaction a diamagnetic ground state of the molecule was concluded[3]. In our present study we can show, however, that the molecule is in fact paramagnetic. Under moderate applied fields the paramagnetic relaxation at iron is relatively slow ($10^8 s^{-1}$).

These experiments were extended to more dilute matrices ($\lesssim$0.1 mole%) than the previous ones (0.1-0.6 mole%) in order to avoid problems with clustering.

2. EXPERIMENTAL

The matrix isolation set-up is shown in fig. 1. The high purity NH_3 gas, which was additionally pre-cleaned from water contamination by cooling, was condensed onto a Be disk (position 1 in fig. 1) cooled by liquid helium. High purity ^{57}Fe was co-deposited from an alumina crucible which was heated via a resistance heated tantalum boat. The proper deposition rates of iron and ammonia were controlled via the change of frequency of oscillating quartz crystals by the deposition and the attenuation of the 6 keV X-ray intensity from a Mössbauer ^{57}Co source. Samples were prepared with concentrations ranging between 0.01 mole% to 0.1 mole% of Fe in NH_3. The pre-vacuum before preparation was better than 10^{-8} torr. The time needed for lay-down of a matrix was typically 1-6 hours leading to Mössbauer absorbers with about 0.005 - 0.1 mg $^{57}Fe/cm^2$. The colours of the doped matrices were whitish pink to metallic brown depending on concentration.

For experiments in applied magnetic fields the absorber was moved down to the center (position 2 in fig. 1) of a superconducting solenoid (B_{max}=5.5T). We used a conventional Mössbauer spectrometer with sinusoidal velocity sweep. The source (^{57}Co in rhodium, about 50 mCi) was moved by a vertical transducer arrangement, with the source at about 10 K. The magnetic hyper-

fine splitting by stray fields at the source proved to be negligible in this configuration.

3 RESULTS

For all studied concentrations the Mössbauer spectra at 4.2 K reveal a quadrupole pattern with parameters close to the earlier found for Fe in NH_3 and NH_3/Xe mixtures[4]. In no case there were found indications of unreacted isolated Fe (with its typical isomer shift of about -0.8mm/s vs. alpha iron[4,10]) or clusters of metallic Fe. For Fe concentrations <0.05 mole% the doublet is riding on a broad but weakly pronounced spectral background which vanishes for T > 20 K (see fig. 2). The quadrupole splitting is constant up to about 120 K. At this temperature the vapour pressure of NH_3 is already 10^{-2} torr and the matrix is gradually evaporating. Whereas at low temperatures the intensities of the two lines of the quadrupole pattern are roughly identical , one finds for matrices kept for prolonged time above 100 K a clearly asymmetric pattern with the line at more negative velocity being stronger (fig. 2). Closer inspection reveals that this pattern is composed of the original doublet and an additional other doublet with slightly higher splitting and isomer shift. The latter doublet has already been found in the earlier studies[4] and was related to the possible formation of a complex with residual impurities in the matrix which occurs upon onset of diffusion at elevated matrix temperatures. We found that this process is indeed irreversible with temperature. In the following only spectra will be considered which do not reveal this additional species.

Fig. 3 shows spectra obtained under various applied external magnetic fields. The matrix temperature was 4.2 K. Note that even at external fields of several Tesla the nuclear moments are not yet polarized along $\vec{B}_{ext}$ (this may be traced from the non-vanishing intensity of the $\Delta I_z = 0$ nuclear transitions).

For the evaluation of the hyperfine spectra we assumed an electronic ground state made up by an effective spin triplet which is split by an axially symmetric crystal field into a doublet and a singlet. The doublet is necessary to describe the magnetic part of the spectra in applied field, the singlet is necessary to account for the pronounced intensity in the center of the spectra especially for small applied fields.

The hyperfine interaction for the spin doublet is described by the following Hamiltonian

$$\underline{H} = \underline{H}_0 + \underline{H}_Q + \underline{H}_{mhf} + \underline{H}_{zee} \qquad (1)$$

$$\underline{H}_Q = \frac{1}{4} e^2 qQ \left[\underline{I}_z^2 - \frac{1}{3} I(I+1) \right] \qquad (1a)$$

$$\underline{H}_{mhf} = \underline{I} \cdot \underline{A} \cdot \underline{S} = A_{\parallel} \underline{I}_z \underline{S}_z + A_{\perp} (\underline{I}_x \underline{S}_x + \underline{I}_y \underline{S}_y) \qquad (1b)$$

$$\underline{H}_{zee} = \underline{S} \, g \, \beta \, \underline{B}_{ext} - \underline{I} \, g_n \, \beta_n \, \underline{B}_{ext} \qquad (1c)$$

$\underline{H}_0$ stands for the electric monopole part of the hyperfine interaction leading to the isomer shift. $\underline{H}_{mhf}$ describes the magnetic and $\underline{H}_Q$ the quadrupolar interactions, $\underline{S}$ and $\underline{I}$ are electronic and nuclear spins, $A_{\parallel}$ and $A_{\perp}$ are the components of the magnetic hyperfine tensor $\underline{A}$ parallel and perpendicular to the z-axis which is locally determined by an axial crystal field, $\frac{1}{2} e^2 qQ$ is the quadrupole splitting (e is the elementary charge, eq the elec-

tric field gradient, Q the nuclear quadrupole moment). The Zeeman Hamiltonian H_{zee} accounts for the electronic and the nuclear Zeeman interaction in the external field $\vec{B}_{ext}$, β and β_n are the Bohr and the nuclear magnetons, the electronic g "tensor" consists of $g_\parallel$ and $g_\perp$ with $g_\parallel/g_\perp = A_\parallel/A_\perp$, g_n is the nuclear g factor. An average over all angles between $\vec{B}_{ext}$ (parallel to the direction of the γ-ray) and the local z-axis as determined by the crystal field was performed.

From the relative population of the crystal field singlet and its decrease under applied field one may estimate the energetic distance Δ between doublet and singlet and the magnetic moment of the doublet (fig. 4). Addition of further spin doublets could certainly improve the quality of fits (fig. 3), the fit results turned out, however, to be of no higher relevance, since the simpler triplet model is already very involved.

The above given Hamiltonian refers to static hyperfine interactions. Relaxation between the electronic levels was allowed in a Wickman-type[11] fluctuation model. This is necessary to describe the transition from fast relaxation ($B_{ext}=0$) to slow relaxation under applied field.

The essential informations from our fits with a spin doublet and a singlet are the following:

i)   the spin doublet is magnetically anisotropic with $g_\perp/g_\parallel \lesssim 0.1$ with a magnetic moment along z of about 6-7 β, the singlet spin state is about Δ = 5-7 K below the doublet for $B_{ext}= 0$ (fig. 4);

ii) the quadrupole interaction is $\frac{1}{2}$ e²qQ = -2 mm/s, independent

of temperature;

iii) the electronic fluctuation rates in applied fields $B_{ext} \gtrsim 0.6T$ are $\lesssim 10^9 \text{ s}^{-1}$;

iv) the hyperfine parameter A corresponds to $B_{hf} = 80$ T if a positive hyperfine field is assumed (B_{ext} adding to B_{hf}), for negative B_{hf} (B_{ext} substracts from B_{hf}) one yields -90 T for high applied fields;

v) the isomer shift is 0.67 mm/s with respect to iron metal at room temperature.

4 DISCUSSION

Solid NH_3 has a cubic crystal structure[12]. Deviations from this stable structure were reported for vapour quenched NH_3 at substrate temperatures around 100 K [13]. The preparations of our matrices were done around 5-8 K. The practically identical Mössbauer spectra of Fe in solid NH_3 and NH_3Xe mixtures[4] show, however, that the symmetry of the surrounding matrix is of no importance for the hyperfine interaction at the iron which rather reflects the electronic state of the small molecule.

By now the structure of $FeNH_3$ is not known. It appears, however, reasonable to assume a point symmetry C_{3v} at Fe with the three-fold axis given by the connection line between Fe and N. The N is closest to Fe, the three H are directed off from the Fe. Under this axially symmetric condition one would expect that for a free iron ion 3d orbitals are of nearly clean σ, π and δ type. Mixtures may occur due to higher symmetry (e.g. cubic) background

fields from the matrix.

Recent MO calculations on similar small molecules (FeH_2O, $CuNH_3$, $NiNH_3$) [14] have shown that the bonding is mainly established by a strong polarization of the cation 4s electrons by the closeby lone pair from the ligand molecule which causes a strong electronic dipolar interaction.

3d-4s and 3d-4p hybridization seem to play a minor role. The iron remains in a nearly atomic configuration. Backdonation from the ligand is expected to be weak.

We now discuss the hyperfine data of $FeNH_3$ and their implications on the electronic ground state of the molecule.

4.1 The isomer shift

The isomer shift of 0.67 mm/s excludes an atomic ground state of Fe close to the usual $3d^6 4s^2$ configuration which has an isomer shift of -0.76 mm/s. From calculated electronic charge densities [15,16] together with the isomer shift data from the various iron species isolated in rare gas matrices [10,17,18] one finds that the atomic electronic configuration with a calculated isomer shift coming closest to the measured isomer shift is $3d^7 4s$ (calculated shift 0.9-1.0 mm/s for electron densities from ref.16, 0.75-0.85 mm/s for densities from ref. 15; a slight negative deviation may be caused by weak back donation from NH_3 to Fe). This atomic configuration can be expected to occur in strongly bound molecules e. g. on surfaces [14].

4.2 The quadrupole interaction

The explanation of the quadrupole interaction with $\frac{1}{2} e^2 qQ = -2$mm/s is not straight-forward. In the axially symmetric molecule one would expect that the 3d states of lowest energy are mainly built up from d_δ orbitals in order to diminish the repulsion from the lone pair of NH_3. In this case any high spin or low spin configu ration with six or seven 3d electrons would result in a strong po sitive quadrupole interaction (one 3d electron with orbital quan- tum number $l_z = \pm 2$ corresponds to $\frac{1}{2} e^2 qQ \approx 4$mm/s [19,20]). Admixtures of wave functions with different l_z e.g. by cubic crystal field contributions might decrease the quadrupole interaction. This, however, appears improbable since the quadrupole interaction is insensitive to the composition and symmetry of the matrix. The contribution to the quadrupole interaction from the lone pair may be estimated from point charge calculation to be at most -0.4mm/s. This value might, however, be strongly increased by the polariza- tion of the 4s electrons away from the lone pair and by popula- tion of the 4p orbitals.

The value of the quadrupole interaction could be formally ex- plained by a configuration $3d^5 \uparrow 3d^2 \downarrow 4s$ with a mixture made up from a state with two spin$\downarrow$ electrons in levels with d_π character with a weight of 2/3 and a state with one electron in d_π and one in d_δ with a weight of 1/3.

The reason why in this case d_π levels are stronger occupied than the d_δ cannot be explained in a free ion model. It is, how- ever, obvious that the simple approximation of a free atom in an axial crystal field cannot reproduce the electronic structure of

Fe in the molecule.

Thermal repopulation of orbitals with different expectation values of l_z apparently play no role up to at least 120 K since the quadrupole interaction is constant.

4.3 The magnetic hyperfine splitting

The application of an external magnetic field results in a big magnetic hyperfine splitting already at moderate applied fields. The saturation value corresponds to 80 T if B_{hf} is assumed to be positive and to -90 T if B_{hf} is negative (fig. 5). In both cases the field dependence of B_{hf} cannot be explained by a Brillouin curve. From the missing polarization of the nuclear moments one concludes that the hyperfine fields caused by the electronic shells are randomly oriented, i.e. that also the atomic moments are not aligned by application of the external field. The appearance of a magnetic hyperfine splitting under these circumstances may have the following reasons:

i) the electronic relaxation of the isolated paramagnetic atoms is slowed down by application of the external field and becomes slower than nuclear Larmor precession ($\approx 10^9 s^{-1}$); the electronic ground state has to be magnetically anisotropic with an anisotropy energy which cannot be overwhelmed by the dipolar interaction with an external field up to 5.5 T;

ii) the $FeNH_3$ molecules are forming magnetic clusters; application of the field may induce a blocking of the magnetization of these clusters or a rise of the ordering temperature to about 5 K; the type of order in clusters has to be antiferromagnetic

or spin-glass like to explain why no alignment of moments is observed in applied field.

Possibility ii) appears improbable for the following reasons: Even matrices with Fe concentrations up to 0.6 mole% show no magnetic hyperfine splitting down to 4 K without application of a field. The studied low concentration matrices also give no magnetic splitting down to 2.5 K. They reveal, however, a broad unresolved background which gradually develops below 20K which is not observed for higher concentrations. This leads us to favour interpretation i). For slow paramagnetic relaxation the field dependence of B_{hf} indeed will not follow a Brillouin curve. The spectra under applied field are then composed by contributions due to the various populated electronic levels with their different hyperfine interactions which are not averaged to an effective splitting. As already indicated it is then necessary to take into account the anisotropy of the magnetic moments for the different electronic levels, i.e. the electronic Zeeman splitting will depend on the angle between applied field and the local preferred anisotropy axis.

An increased Zeeman splitting apparently slows dow relaxation whereas only weakly split levels are still relaxing fast as in the case without field thus exhibiting only the quadrupole doublet. This can explain part of the strong intensity in the center of the magnetic patterns especially in small fields.

Note also that in the case of nearly uniaxial anisotropy one may expect that the Zeeman interaction at ions with the anisotropy axis at angles around 90° with respect to $\vec{B}_{ext}$ is very weak. In lack of a picture of the electronic level scheme of the iron

in $FeNH_3$ had to make an ad hoc assumption for the evaluation as described by the effective Hamiltonian introduced above. For $B_{ext} \gtrsim 3T$ it was in principle sufficient to assume an effective spin 1/2 doublet with slow relaxation. For smaller fields, however, an increased relaxation rate and population of fast relaxing other spin states had to be included (for simplicity we introduced only one singlet) which are not populated for stronger Zeeman splitting. The relaxation rate of the spin doublet varies from $10^9 s^{-1}$ to $10^8 s^{-1}$ for B_{ext} varying from 0 to $\gtrsim 3$ T. These numbers have, however, only qualitative character since they are very model dependent. Following facts need closer discussion:

a) the magnitude of the hyperfine field

b) the magnetic anisotropy of the electronic ground state

c) the reason of slow relaxation

a) The magnetic hyperfine field is relatively large compared to those commonly met for iron compounds. It is, however, quite close to those of other matrix-isolated species like atomic $Fe(3d^6 4s^2)$, $B_{hf} = 83$ T [7], and the dimer Fe_2, $B_{hf} = 66$ T [8].

The origin of these large hyperfine fields is the strong contact contribution by the 4s electrons. One 4s↑ electron produces a hyperfine field of the order of 200 T [9]. A negative hyperfine field of −90 T which also can describe the data may arise from a 4s electron with opposite spin. Instead of a quintet (for 4s↑) the spin state would then be a triplet. In fact MO calculations[14] for FeH_2O showed that the triplet is energically more favourable. In this case, however, the negative contact contribution has to be strong enough to overcome the orbital contributions which are positive[21].

b) The strong magnetic anisotropy of the electronic ground state $(g_\perp/g_\parallel \lesssim 0.1)$ is in contradiction to an orbital singlet ground state. This would be expected for a $3d^5\!\uparrow\ 3d^2\!\downarrow\ 4s\!\uparrow$ (or $4s\!\downarrow$) configuration with the $3d^2\!\downarrow$ in a d_π or d_δ like doublet. A finite anisotropy may, however, arise from a population of both d_π and d_δ states which has already been inferred when discussing the quadrupole interaction. I.e. there is also a contribution by an orbital quartet.

The spin state would be in any case a quintet for $4s\!\uparrow$ (triplet for $4s\!\downarrow$). In this case one may describe the electronic ground state by an effective spin 2 (or 1) multiplet which is split by the a-xial crystal field which arises from the non-vanishing orbital mo-mentum of the orbital quartet.

The crystal field levels are then two (or one) uniaxial doublets and a singlet. According to the strength of the anisotropy the overall splitting by the crystal field should be > 10K. This is higher than the estimate for the energy difference between the spin singlet and the doublet in our simplified model (effective spin 1) but in accord for an order of magnitude guess. The mag-netic moment estimated for the axial doublet from our data ($\sim 7\ \beta$) also hints to a relatively high spin and a non-vanishing orbital momentum.

Fits to the data with the assumption of a spin quintet are not very sensitive but reproduce the results as well as the above as-sumed simpler model with a triplet.

c) The rapid transition from fast to slow electronic spin relaxa-tion under applied external field is surprising. The fast relaxa-tion without applied field firstly shows that the orbital momentum in the ground state cannot be completely quenched and secondly

that a conjugate spin doublet is improbable to be the lowest crystal field state. In this case one rather would expect an increase of spin lattice relaxation rate for the direct process[22] upon application of the external field which is not observed. The slow down of relaxation may, however, be explained in the above sketched model. If the spin singlet is the lowest state and the magnetic doublet is several K higher in energy one will observe a non-magnetic pattern down to low temperatures. In applied field the Zeeman splitting will bring one component of the doublet below the singlet and the indirect processes between them will slow down exponentially. This may happen already at moderate fields since the magnetic moment of the doublet is high.

5 CONCLUSION

We have studied highly dilute solutions of iron in solid ammonia. The reaction product $FeNH_3$ is paramagnetic. The high value of the magnetic hyperfine field found under external applied field together with the value of the isomer shift point to a nearly atomic configuration of iron $3d^74s$. The strong axial anisotropy speaks against a pure singlet orbital groudstate. The Mössbauer spectra under applied field can be described by a superposition of the spectra due to a spin singlet and a doublet with a magnetic moment 7 β with the singlet lying below the doublet for zero external field. The observed slow paramagnetic relaxation under applied field can be explained in this model by the slow down of indirect processes. A higher spin multiplicity (e.g. a quintet) cannot be ruled out.

The information on the electronic ground state derived from

the hyperfine data may be taken as test for first principle molecular orbital calculations for the small molecule $FeNH_3$. Calculations of this type are under progress[23].

ACKNOWLEDGEMENTS

FIGURE CAPTIONS

Fig. 1 - Matrix-isolation cryostat, the sample is moved from posi‐ tion 1 (preparation) to position 2 (Mössbauer measurement in applied magnetic field) by a gear drive system sealed by bellows.

Fig. 2 - Mössbauer absorption spectra of 0.04 mole% Fe in solid NH_3 at different temperatures (source: ^{57}Co in Rh at 10 K).

Fig. 3 - Mössbauer absorption spectra of 0.04 mole% Fe in solid NH_3 at different applied magnetic fields B_{ext} (directed parallel to the γ-ray).

Fig. 4 - Simplified model of the atomic spin levels of Fe in $FeNH_3$ used for data analysis.

Fig. 5 - Field dependence of the magnetic hyperfine field B_{hf} at 4.2 K (+,- refer to positive and negative B_{hf}, respecti‐ vely). For comparison the drawn line gives a Brillouin curve for g=2, S=7/2 and a saturation value of 80 T.
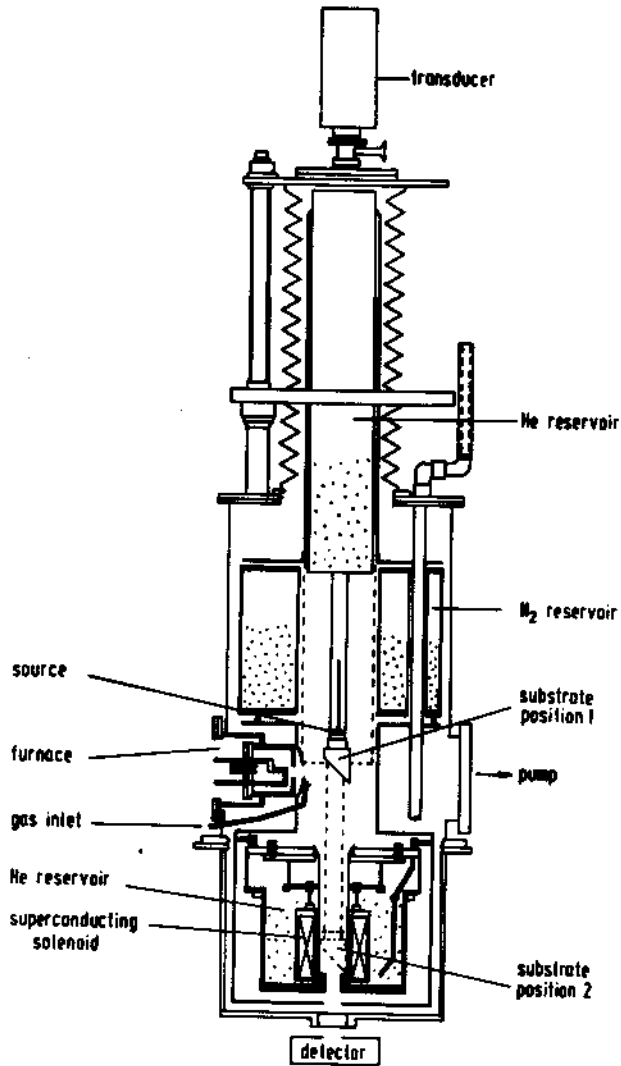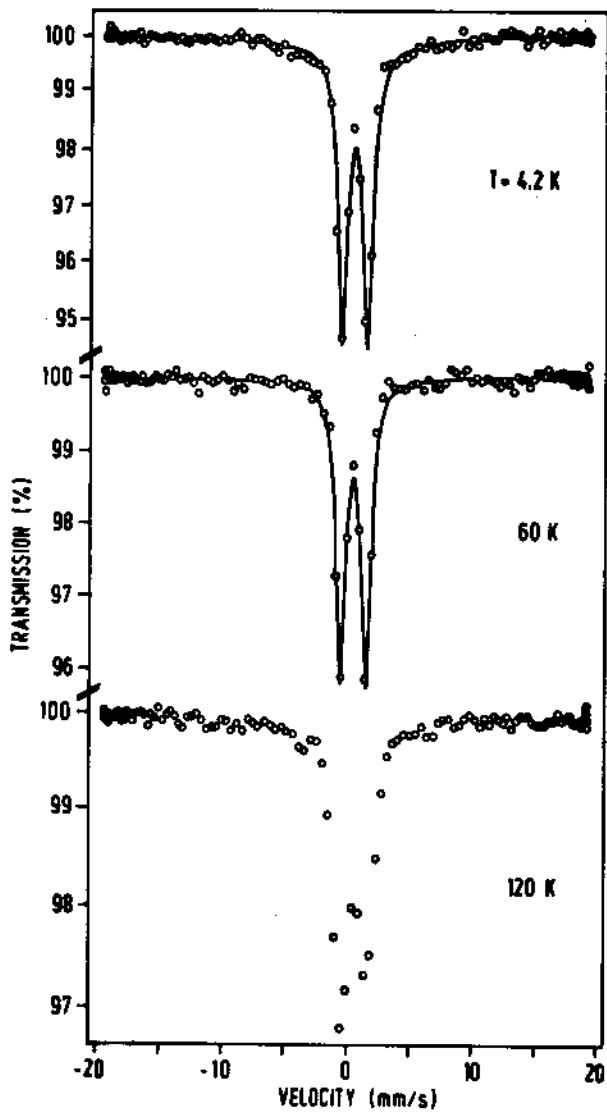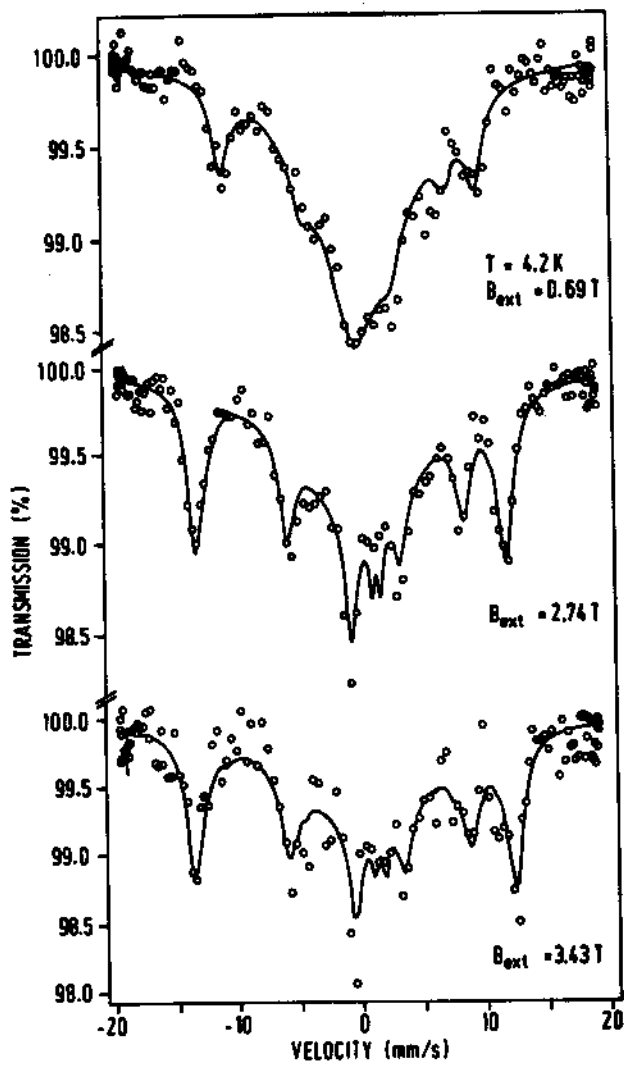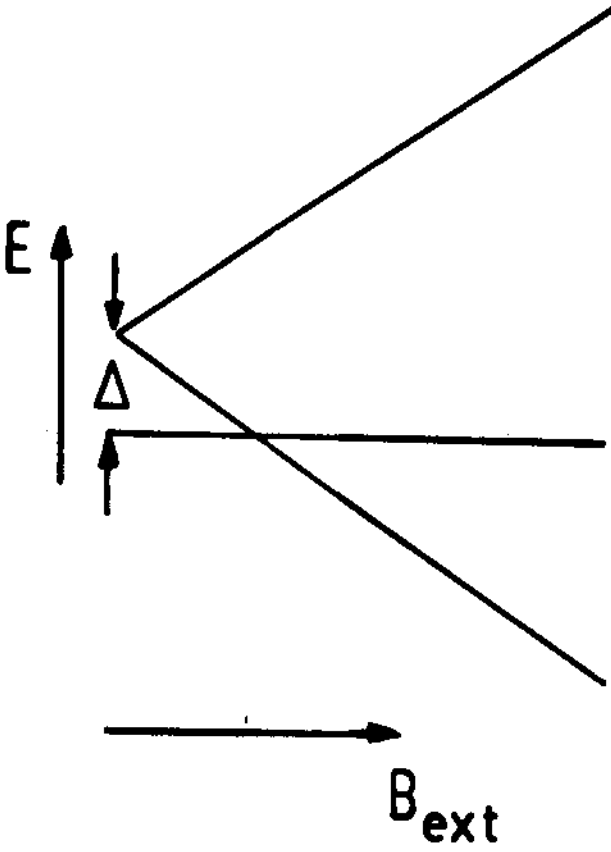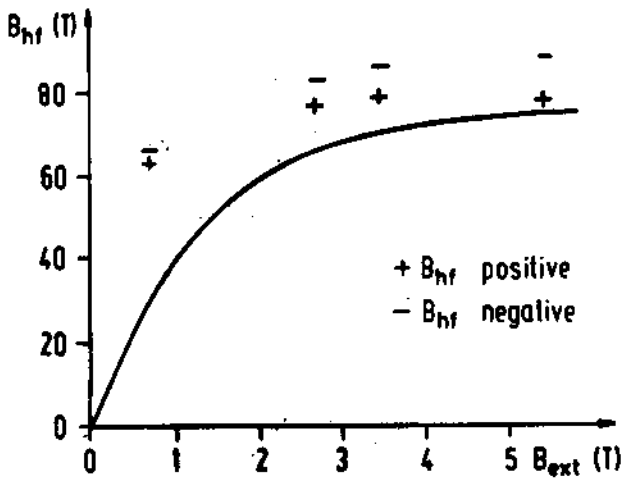
Fig. 1

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Fig. 5

REFERENCES

1. H. Micklitz, in Matrix Isolation Spectroscopy, edited by A.J. Barnes, W.I. Orville-Thomas, A. Moller and G. Gaufree (Reidel, Dordrecht, 1981) p. 91.

2. M. Pasternak, Hyp. Int. 27, 173 (1986).

3. P.H. Barrett and M. Pasternak, J. Chem. Phys. 71, 3837 (1979).

4. E. Baggio Saitovitch, F.J. Litterst and H. Micklitz, Chem. Phys. Lett. 83, 622 (1981).

5. See e.g., Cryochemistry, edited by M. Moskovits and G.A. Ozin (John Wiley, N.Y., 1976).

6. See e.g., Chemisorption and Reactions on Metallic Films, edited by J.R. Anderson (Academic Press, London, N.Y., 1971).

7. P.A. Montano, P.H. Barrett and Z. Shanfield, Solid State Commun. 15, 1675 (1974).

8. P.A. Montano, P.H. Barrett and Z. Shanfield, J. Chem. Phys. 64, 2896 (1976).

9. P.A. Montano, P.H. Barrett, H. Micklitz, A.J. Freeman and J.V. Mallow, Phys. Rev. B17, 6 (1978).

10. T.K. McNab, H. Micklitz and P.H. Barrett Phys. Rev. B4, 3787 (1971).

11. H.H. Wickman, in Mössbauer Effect Methodology, edited by I.J. Gruverman (Plenum, N.Y., 1966) Vol. 2, p. 64.

12. J. Olovsson and D.H. Templeton, Acta Cryst. 12, 832 (1959).

13. P.A. Staats and H.W. Morgan, J. Chem. Phys. 31, 553 (1959).

14. C.W. Bauschlicher Jr., J. Chem. Phys. 84, 260 (1986).

15. J.L.K.F. de Vries, J.M. Trooster and P. Ros, J. Chem. Phys. 63, 5256 (1975).

16. A.J. Freeman and D.E. Ellis, in Mössbauer Isomer Shifts, edited by G.K. Shenoy and F.E. Wagner (North Holland, Amsterdam, 1978) p. 137.

17. H. Micklitz and P.H. Barrett, Phys. Rev. Lett. 28, 1547 (1972).

18. H. Micklitz and F.J. Litterst, Phys. Rev. Lett. 33, 480 (1974).

19. R. Ingalls, Phys. Rev. B188, 1045 (1969).

20. S.N. Ray and T.P. Das, Phys. Rev. B16, 4794 (1977).

21. A.J. Freeman and R.E. Watson, in Magnetism, edited by G.T. Rado and H. Suhl (Academic Press, N.Y., 1965), Vol. IIA. p. 167.

22. R. Orbach, Proc. Phys. Soc. (London) A77, 821 (1961).

23. Joice Terra and Diana Guenzburger: to appear in Phys. Rev. Jan. 1989.