

Advanced Experiments
II. Physikalisches Institut
Universität zu Köln

Experiment M2.6

Electron Spin Resonance

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Translation to English

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Preparations

- Electronic structure of atoms (Quantum numbers, degeneration and 3D distribution of the orbitals, especially the d-orbitals)
- Electronic configuration of Cu and Cu²⁺
- Dia- and para-magnetism
- Paramagnetic resonance, Zeeman effect
- Microwave techniques (microwave conductance, resonator)

Introduction

Electron spin resonance (ESR) is a spectroscopic method, which probes the energy level of the paramagnetic electrons (no long range order) in an applied field. In field of a few thousand Gauss (kG) it is possible to examine these transitions using an electromagnetic wave of microwave size ($\lambda \sim \text{cm}$). From an ESR measurement it is possible to extract information on the Landé factor (g-factor), the fine- and hyperfine structure of the valence electrons (the outmost shell), as well as the coupling mechanisms involved between the magnetic dipoles present in the examined compound.

In this experiment, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ will be used to learn more about the ESR technique. The goal is to measure spectra from a powder and a single crystal and to evaluate the data, from which we can gain the directional components of the g-factor within a crystal plane and a along the axis perpendicular to it. These data can be related to the coordination and next surrounding of Cu in the mentioned compound. The broadness and shape of the resonance curves will also be used to deduce information about the spin to spin interactions.

Paramagnetic Resonance

A closed cycle current creates a magnetic dipole that originates from spin and orbital moments in the electronic shell. However, only half filled orbitals contribute to the total moment, because full orbitals contain two electrons, which cancel each others' moments. The total moment can be calculated by using Hund's rules. In the first row transition metals, only the electrons in the 3d orbitals have relevance for the magnetic properties.

The connection between orbital and magnetic moment is defined in the g-factor:

$\mu = -g\mu_B J$. This equation is valid for a free atom (ion).

In a solid state compound, each atom is affected by the electric field of the neighboring atoms, normally called the crystal field. If the crystal field is stronger than the spin-orbit coupling, Hund's third rule is neglected. This means that the orbital moment L is suppressed and the total magnetic impulse (J) from the electrons is equal the total spin (S). Furthermore, the crystal field leads to a vector like g-factor, which depends on the direction through the crystal (a tensor). An outer field destroys the degeneracy between spin states with equal impulse quanta (J), the Zeeman effect, since the energy is dependent on the J -direction compared to the outer field. As the impulse is a pure quantum number, the magnetic moment m in a magnetic field will be one too and there are only a narrow number of states. Using electromagnetic waves it is possible to perform excitation between these individual states. For this to happen, the magnetic field has to be

perpendicular to the excitation field, coming from the radiation source and the possible states are $m = \pm 1$. A transition between the states occurs when the incoming energy is equal to the energy gap between two neighboring states. In the excitation process a light quantum is absorbed, which is short thereafter emitted again. In thermodynamic equilibrium, the number of excited states is given through the Boltzmann statistic. An accurate description can be found in references [1,4,5] in chapter 3.

Bloch's equation

Bloch's theory gives a macroscopic description of the magnetic resonance, in which a whole ensemble of magnetic dipoles is treated. The relevant physical parameter is the magnetisation M , which is the sum of all dipole moments in a defined volume:

$$M = \sum_{Vol} \mu_i$$

As in the description of one magnetic moment in a constant field H_0 , the total magnetisation is deduced as follows: $\frac{dM}{dt} = -\gamma M \cdot H_0$

If a time dependent field is added, it is necessary to modify the equation with a relaxation term, which describes a continuous change towards thermodynamic equilibrium. Analogue to the theory of harmonic oscillation, the process to reach equilibrium is exponential towards the equilibrium value M_0 . The process can be described with two time-constants, T_1 and T_2 .

Only the interaction between the magnetic dipole and its surrounding is a possible way of changing the energy of the dipole. This is called spin-lattice interaction, because the lattice works as an energy storage. The relevant time for the interaction is called the longitudinal relaxation time (T_1).

The presence of a perpendicular magnetic relaxation can be interpreted as a phase coherence of spin dipole moments. Changing this component affects the phase relation between the dipoles, however, the system energy stays constant. This interaction is treated as the transverse relaxation time (T_2).

The total dipole movement equation is defined as (H_0 is along z):

$$\begin{aligned} \frac{dM_z}{dt} &= -\gamma [M \cdot H]_z + \frac{M_0 - M_z}{T_1} \\ \frac{dM_{x,y}}{dt} &= -\gamma [M \cdot H]_{x,y} + \frac{M_{x,y}}{T_2} \end{aligned}$$

The shape of the resonance curve originates from the solution of the Bloch's equations.

Curve shape and broadness

The natural curve shape and broadness is mainly given by the Heisenberg uncertainty relation: $\Delta E \Delta t \sim \hbar$.

The lifetime of the specific states Δt is in this case the relaxation rate of T_1 , which is dependent on the spin-lattice interaction, resulting in a Lorentz like resonance curve.

Because of additional spin to spin interactions (not valid for diluted systems), there will also be the T_2 relaxation time und, therefore, the ESR spectrum contains more processes resulting in line broadening at the resonance.

The possible spin interactions are, furthermore, the dipole-dipole interaction and the (super-)exchange interactions.

Dipole-dipole interactions

The dipole-dipole interaction is of magnetic nature. Any magnetic dipole creates a local magnetic field at the distance r equal to: $H_{loc} = \frac{\mu_B}{4\pi r^3}$. A second dipole, at distance r , feels the modified H-field and the resonance energy is shifted. This causes the resonance to seem broader than expected. The dipole-dipole interaction is not only dependent on the distance r (a Bohr magneton at the distance 3 Å creates a field of about 400 G, but at a distance of 6 Å only 50 G) but also on the orientation of the neighboring spins. As a result, the spin orientations in space will affect the resonance curve to be either more Gauss or Lorentz like.

The interaction between unlike spins is dominated by the so called inhomogeneous statistical broadening. In this case, the local dipole magnetic fields are evenly distributed (Gauss). The result is, of course, that the curve becomes more Gauss like. With identical spins, which also precede with the same Larmor frequency, a dynamical coupling appears; if the local field, H_{loc} , oscillates with the same frequency as the spin at the local site, there is a possibility that the spin changes its direction. The Larmor frequency phase between the magnetic dipoles is lost but the Zeeman energy and also the resonance frequency stay the same. The curve becomes more Lorentz like and it is called dynamic homogeneous curve broadening.

Exchange interactions

In paramagnetic substances and above a certain concentration of spins the curve shape is dominated by spin to spin exchange interaction.

The exchange interactions are electrostatic and result from the Pauli principle, which is activated through the superposition of the electron wave functions of different atoms. There are several different exchanges; the direct exchange originates from superposition of orbitals of two neighboring paramagnetic atoms. The indirect exchange, also called super-exchange, appears if there is a diamagnetic atom between two paramagnetic atoms and works as a conducting bridge, prolonging the common electronic wave function. The energy of both interactions can be described according to: $H_{1,2} = -2J \cdot S_1 S_2$ with the exchange integral J .

The exchange interactions lead to a narrowing of the resonance curve, as shown in Fig.1. It is possible to describe the event as follows: the exchange interactions causes a spin coherence in space, which lowers the number of possible frequencies, due to very similar local fields, H_{loc} . A full explanation of this effect can be found in [1]. The shape of the resonance curve changes as follows: the area under the curve stays constant, but turns more Lorentz like.

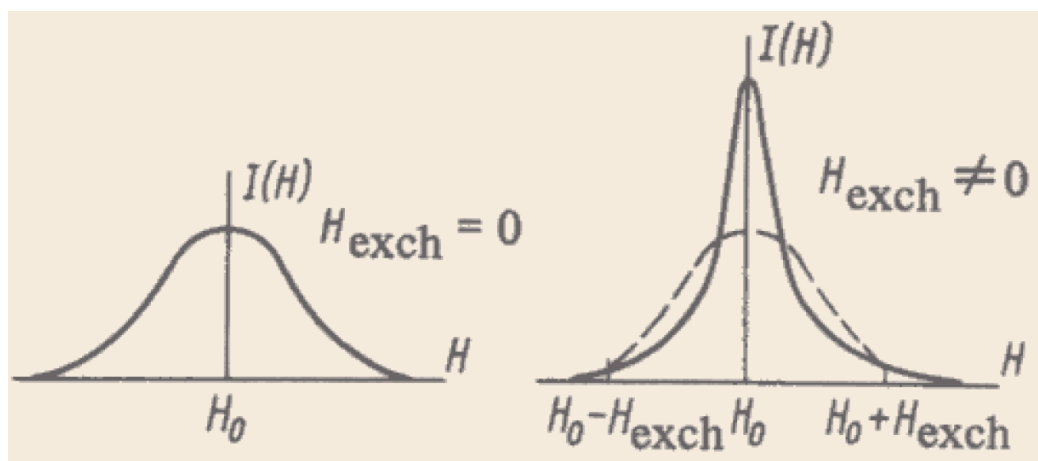


Fig.1 The narrowing of the resonance curve as exchange interactions set in.

For spins having different magnetic moments, both dipole-dipole broadening and a exchange narrowing can occur simultaneously. The resulting curve shape is then depending on the strengths of the different effects.

A special case is a strong exchange interaction between two single electron ions. This leads to a cancellation at the individual g_1 and g_2 but a narrowing of the curve for the common resonance at $g = (g_1 + g_2)/2$.

For further reading see Chap. 4 in [2] and Chap. 6 in [3].

Coppersulfate-pentahydrate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$)

The unit cell of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ contains two individual Cu^{2+} sites. Both ions coordinate four negatively charged oxygen ions that originate from H_2O molecules and create a square planar arrangement (the Cu to O distance is approx. 2.8 Å). Furthermore, two other oxygen, belonging to SO_4^{2-} ions, are found on a line perpendicular to the plane on either side of the Cu^{2+} ion. The closest surrounding of the Cu^{2+} is thus an octahedron, which is elongated in one direction and the symmetry is lowered to tetragonal. The crystal field on Cu^{2+} is thus strongly anisotropic. Both the Cu sites have close to equal coordination, however, the two tetrahedral units are found at a relative angle of about 98°.

Through investigations of the g -Tensor, it is possible to draw conclusions on the local structure surrounding Cu in the solid state compound e.g. the local symmetry. Does the local structure in $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ have an effect on the g -Tensor of Cu^{2+} ? (see [4,5])

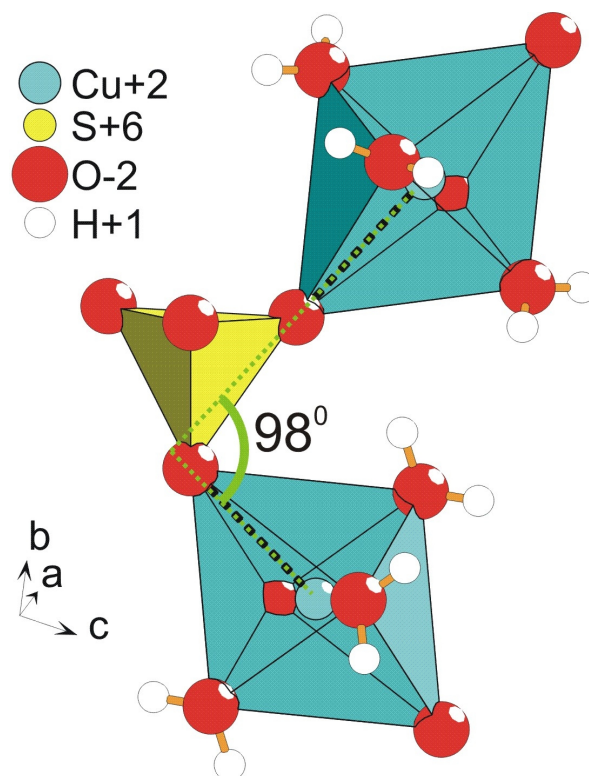


Fig.2 A perspective view of the $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ structure with indicated angle (dashed line) between the two Cu sites and their tetragonal axes.

The degeneracy of single electron states with the same impulse quantum number l (do not compare this with the many electron impulse quantum state J !) is at least partly cancelled out. The five different 3d orbitals split, in an octahedral crystal field, into two levels with different energies i.e. the levels t_{2g} and e_g . The t_{2g} level is energetically more favorable and three-fold and the higher e_g level has a two-fold degeneracy. Through a tetragonal distortion, these level are further split into four different levels of energies.

What does the orbital splitting look like for Cu^{2+} in $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$?

ESR-Experimental

The ESR spectrometer consists of the following parts (Fig.3):

- 1) Watercooled electromagnet with generator. Generates fields between 0 and 6 kG.
- 2) Microwave equipment: Klystron, microwave bridge, resonator, and detector
- 3) Data amplifier and recording.

The sample is placed between the two poles of the electromagnet inside a cavity resonator (Fig.3 – why do we need a resonator?). The sample absorbs energy in form of microwaves from the Klystron, if the resonance conditions are fulfilled. The energy loss registered by the detector and the signal is recorded as a voltage.

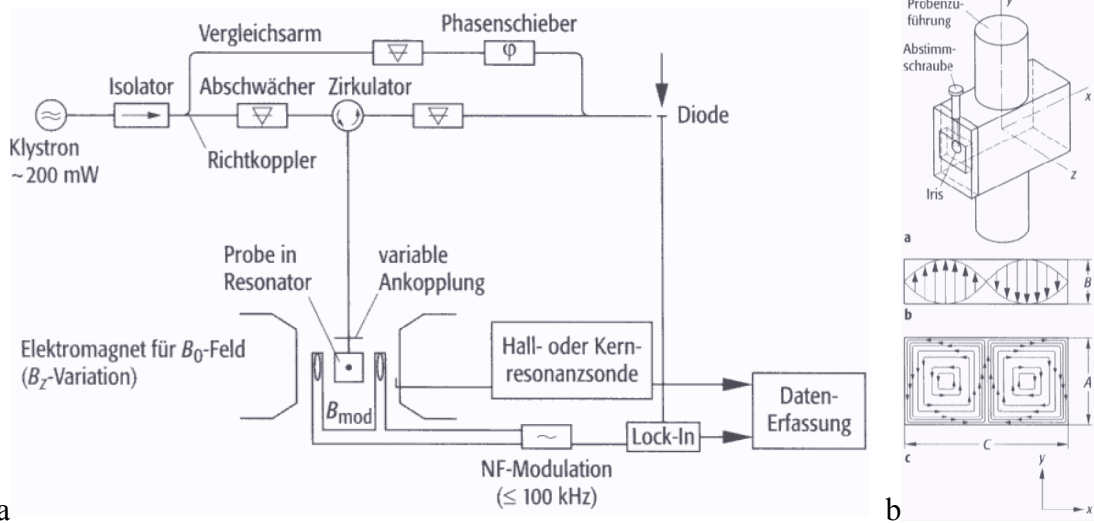


Fig.3 (a) The experimental setup of an ESR spectrometer. (b) The resonance cavity and the distribution of the standing electromagnetic wave inside.

Notes on the measuring technique:

During ESR measurements the wavelength is kept constant, but the large DC field is scanned (why?). In our experiment, the frequency used is about 10 GHz (corresponding to a wavelength of about 3 cm).

The field strength is measured with a Hall probe, attached directly between the magnetic poles, throughout the experiment.

If the measurement would be done with the described equipment, the signal would be a weak DC current. The problem is that background noise produces a similar signal and it would be difficult to separate them unless a further help is at hand: the static field at the site of the sample is modulated by a small AC field, controlled by a Lock-in amplifier (Fig.3). The sample reacts to the modulated magnetic field and the produced signal becomes sinusoidal. The amplitude of the signal change corresponds to the variation of absorbed energy in the resonator cavity. Now, the signal is of AC type and can be “filtered out” by the Lock-in amplifier and enlarged enough to be well separated from the noise, since the phase and frequency of the signal is known. Instead of an absorption signal, the recorded data are the derivation from the absorption (Fig.4).

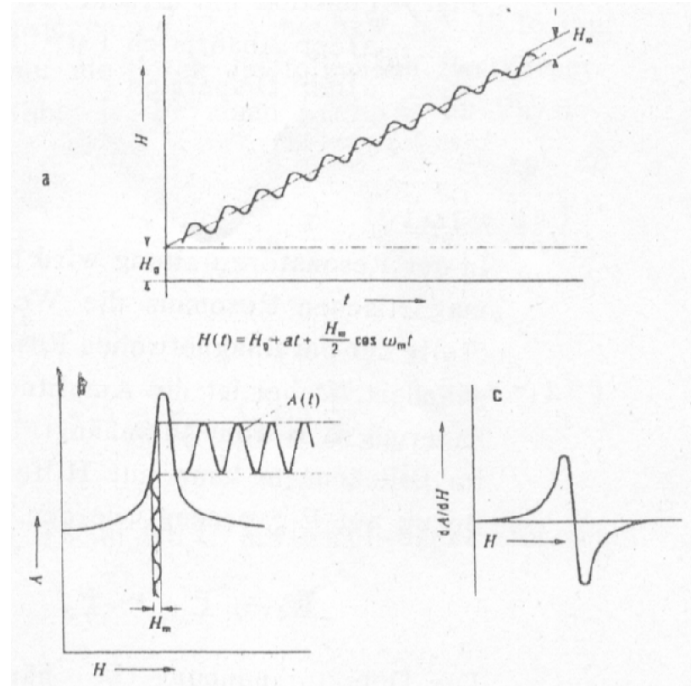


Fig.4 The modulation of the outer DC field and its influence on the shape of the resonance curve.

Absorption and Dispersion

In ESR, the sample behavior can be described through its complex high-frequency susceptibility: $X = X' - iX''$

The absorption from the microwave field is proportional to the imaginary X'' part and the real part X' represents the dispersion.

If no resonance is at hand, the resonator will reflect the waves with the field strength F_0 . At the resonance, this changes with the size $\Delta F(X)$, resulting in a wave field strength of $F_1(X) = F_0 + \Delta F(X)$. The change in amplitude of $F_1(X)$ is proportional to X'' and the phase change is related to X' .

In the bridge arm, F_1 is conducted and reflected so that the signal wave can interfere with a reference wave giving $F_{tot} = F_1 + F_2$, where F_2 is the reference wave. The change in the diode (detector) voltage is proportional to the amplitude change of F_{tot} . During the measurement, the phase of F_2 is adjusted in the reference arm (Fig.3) so that the signal in the detector is proportional to the amplitude of $\Delta F(X)$. This happens when F_0 and F_2 are in-phase or out-of-phase.

If the phase difference, between F_0 and F_2 , is $\pi/2$, the detector signal will be mainly sensitive to the dispersion.

Experimental work and evaluation

The task is to measure a single crystal of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ as a function of angle between outer field and the chosen crystal axis (all 10° between 0° and 180°). Also, a powder sample, of the same compound, will be measured for comparison.

All curves should be presented in the logbook!

The line shape of the curves should be examined. One of the resonance curves, from the single crystal data, should be compared with Gauss and Lorentz functions to extract the full-width-at-half-maximum (FWHM). The fitting parameter should all be presented in the logbook. The shape of the powder sample curve should be compared to those in ref. [5].

Also, the resonance and peak broadness from the all ESR single crystal data should be calculated and presented. The extracted g-factors and FWHM values must be presented as a function of crystal-to-field angle. Both the g_\perp and g_\parallel have to be extracted from the powder data.

Finally, the powder- and single crystal data should be compared with one-another and with literature. A discussion of the results is obligatory including a notification on error sources and their approximate sizes.

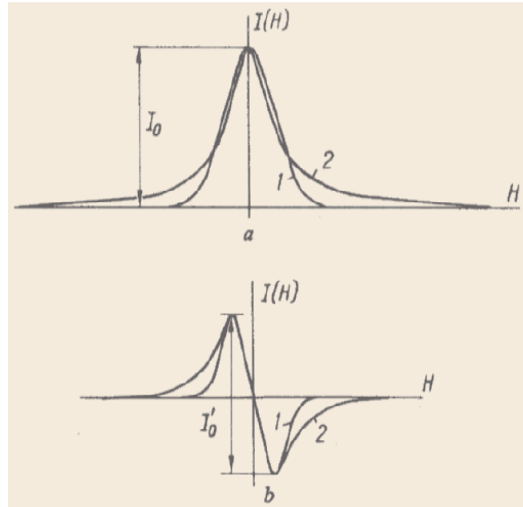


Fig.5 Shape comparison of Gauss(1) and Lorentz(2) curves and their respective derivatives.

For the FWHM of the integrated curves, the following is valid:

$$\text{Gauss} = \frac{\Delta H_{1/2}}{\Delta H_{pp}} = (2 \ln 2)^{1/2}$$

$$\text{Lorentz} = \frac{\Delta H_{1/2}}{\Delta H_{pp}} = 3^{1/2}$$

References:

- [1] J.H. Van Vleck, Phys. Rev. 74 (1948) 1168
- [2] L.A. Sorin, M.V. Vlasova, "Electron spin Resonance of Paramagnetic Crystals", Plenum Press 1973 – available in the library at 2nd Institute of Physics
- [3] G.E. Pake, T.L. Estle, "The Physical Principles of Electron Paramagnetic Resonance", Benjamin, Inc. Reading 1973 – available in the library at 2nd Institute of Physics
- [4] J. Wheatley, D. Halliday, "Paramagnetic Absorption in Single Crystal of Cupper Sulfate Pentahydrate", Phys. Rev. 75 (1948) 1412-1415
- [5] F.K. Kneubühl, "Line Shapes of ESR Signals Produced by Powders... ", J. Chem. Phys. 33 (1960) 1074-1078

Further reading

- [6] T. Mayer-Kuckuk, "Atomphysik"
- [7] Ch. Kittel, „Einführung in die Festkörperphysik“, Kap. 14,16
- [8] R.P. Feynman, Lectures on Physics, Ch.23
- [9] D.M.S. Bagguley, S.H.E. Griffiths, „Paramagnetic Resonance in Copper Sulfate“, Proc. Roy. Soc. A 201 (1950) 366-377
- [10] Lexikon der Physik, Spektrum Akademischer Verlag 1998

Questionnaire for the M-practical course

Electron spin resonance

Please fill in the form after you finished the experiment and discuss the criticism with your tutor wherever applicable.

The valuation is based on the german school mark system (1:best – 6:worst)

Semester: Winter 20__/_ Summer 20__

Query 1:

How much did you learn from the experiment in terms of concepts in physics as well as technical skills?

[illegible]

Query 2:

How do you rate the quality of the experimental equipment?

[illegible]

Query 3:

Is the experiment up-to-date with recent topics in physics?

[illegible]

Query 4:

What is the advance in your experimental skills?

[illegible]

Query 5:

Did you have fun carrying out the experiment?

[illegible]

Query 6:

Is the tutorial of the experiment explicit?

[illegible]

Query 7:

How much time did you invest in the preparation?

h

Query 8:

How do you assess the experiment in total?

[illegible]







study course:	Master <input type="checkbox"/>	Teacher <input type="checkbox"/>
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Comments and suggestions

Overall mark for your tutor

Name of your tutor: _____

[illegible]

Workplace:	Operating instruction according § 20 GEFSTOFFV	As at 4/2011 <i>Date:</i> 18.04.2011
<h2>High magnetic fields</h2>		
Physical Danger: Any freely movable objects could be pulled into the magnetic field and may reach high velocities by this. High magnetic fields may damage magnetic data storage media like hard disks or credit cards and may lead to loss of information.		    
Danger to health: High magnetic fields can impair the proper function of cardiac pacemaker and other electronic implants.		
Safety instructions: Keep precision mechanical devices like watches and magnetic data storage media like computer hard disks, cards with magnetic stripe or floppy disks in sufficient safe distance from the magnet.		
Technical measures: - Organizational measures: Before running the magnet remove all parts that might be attracted by the magnetic field from its surrounding.		
Behavior in case of danger: In case of injuries caused by parts attracted by the magnet provide first aid.		
First aid: Emergency number: Emergency medical services: 01-112 Nearest Hospital: 01-4792213 Evangelisches Krankenhaus, Weyertal 76, 50931 Köln Maintenance main building: 2200		
Proper disposal -		
<i>If necessary: * Specify location</i>		<i>(Signature)</i>