We will now explicitely include damping in our model. Therefore, we rewrite the equation of motion, this time using the electron velocity v:

$$m_0 \frac{dv}{dt} + m_0 \gamma v = -eE$$

For the case of free electrons, it is often more intuitive to think of the damping time τ instead of the damping rate: $\tau = 1/\gamma$

$$m_0 \frac{dv}{dt} + m_0 \cdot \frac{1}{\tau} \cdot v = -eE$$

The solution for v must have a similar form as the solution for x. With the ansatz $v = v_0 e^{-i\omega t}$, one obtains:

$$v(t) = -\frac{e\tau}{m_0} \frac{1}{1-i\omega\tau} E(t)$$

For the case of free electrons, one can also use the current and the conductivity to describe the behavior of the electrons. We have Ohm's law: $j = -Nev = \sigma E$

(j: current, σ: conductivity)

$$\Rightarrow \quad j = \underbrace{\frac{Ne^2\tau}{m_0} \frac{1}{1-i\omega\tau}}_{\sigma(\omega)} E(t)$$

$\sigma(\omega)$ AC conductivity (optical conductivity)

We can define $\sigma(\omega) = \sigma_0 \cdot \frac{1}{1-i\omega\tau}$

with $\sigma_0 = \frac{Ne\tau}{m_0}$

The optical conductivity and the dielectric function are related to each other by

$$\varepsilon_r(\omega) = 1 + \frac{i\sigma(\omega)}{\varepsilon_0 \omega}$$

slide

Roughly speaking, ε_r is used for high frequencies and σ for low frequencies where the relation to the DC conductivity σ_0 becomes very obvious.

To further understand the optical properties of metals, let us look at some numbers. The plasma frequency depends on the number density of free electrons: $\omega_p = \sqrt{\frac{N_e^2}{\varepsilon_0 m_0}}$

The slide shows an overview of selected values for N, ω_p, and λ_p. It is apparent that very large values of N lead to plasma frequencies in the ultraviolet spectral region. Above this frequency, metals become transparent. An example is Aluminium slide.

An important mechanism of absorption in metals are <u>interband transitions</u>. Here, a photon moves an electron from an occupied to an unoccupied band. Let us discuss this for our example of Al. The slide shows the band diagram (we have already encountered this before. When you look closely, you can see the back folded free electron bands).

The absorption rate is proportional to the density of states in the final state

in [illegible]. This is Fermi's golden rule:

$$W_{i\to f} = \frac{2\pi}{\hbar} |\langle f|H'|i\rangle|^2 S$$

DOS in final state

We thus have strong adsorption for energies corresponding to a transition between a initial state with a high density and a final state with a high density.
This is the case if the bands are parallel (only direct transitions have to be considered due to the small k of the photon).
Two such transitions are marked in the diagram. They cause the dip in the reflecting of Al at 1.5 eV. The overall slightly decreased reflectivity above 1.5 eV is caused by higher inter band transitions which are not so pronounced due to the absence of the parallel band effect.
Our second example is copper. Here, in addition to the s-bands found in Al, the d-bands are important [slide]. The 3d band has a pronounced and narrow maximum as the overlap between the d-orbitals is small. Consequently, absorption will increase significantly for energies where intra band transitions from the 3d band are allowed. This can be also seen in the full band structure. [slide]. The experimental curve for the reflectivity thus drops of significantly even well before the plasma

edge (slide). The onset of the intraband transition above 2 eV explains the red color of copper. The same argument explains the yellow color of gold (slide). Example: (slide)

Now we consider the behavior of the free electrons right at the plasma frequency. Remember, that a plasma consists of a gas of charged particles in dynamic equilibrium. The particles are in constant motion, and this can create local charge fluctuations. When by such a fluctuation a small region with an excess charge is created, a force is acting on these electrons with the goal of reaching a homogeneous distribution again. The velocity acquired by the electrons can lead to overshooting and in consequence to an oscillatory motion, the <u>plasma oscillation</u> which have their characteristic frequency right at the plasma frequency. The corresponding quasiparticle is called <u>plasmon</u> (slide). As the plasmon is a longitudinal wave, it cannot couple with photons, which are described by a transversal wave. In the next lecture we will see that they can be detected by inelastic scattering of photons instead. This situation changes for a special plasmon mode localized at the surface

of a metal, the surface plasmon. [slide].
The associated wave propagates along the interface. The amplitude of the electric field decays exponentially on either side of the interface. It is obvious that the surface plasmon contains also transverse components of the electric field that allow coupling to photons. In the case of strong coupling it is appropriate to speak of a polariton which is a coupled electric polarization – photon wave. The most clear manifestation of surface plasmon effects is found in the optical properties of metal nanoparticles. The color of a suspension of such clusters is dominated by the plasmon resonance. This is exploited since antiquity to produce colored windows by embedding metal nanoparticles.

Quasiparticle scattering

In the last chapter we have encountered the plasmon as a quasiparticle describing a collective excitation of the free electron gas. In this chapter we will see, how the plasmon and other quasiparticles can be detected via scattering with photons, electrons, or neutrons. But let us start with a brief review on the most important quasiparticle, the phonon.

Excitations of vibrations in the lattice can be described by phonons. The complex patterns of vibrations can then be treated as a superposition of these elementary excitations (slide)

The dependency of wave vector and frequency is given by the phonon dispersion relation.

The standard model system to describe phonons is the linear diatomic chain. (slide). Note that a meaningful wave vector can only be defined inside the first Brillouin zone as otherwise the wavelength does get shorter than the unit cell, which is not meaningful as the crystal lattice is discrete. (slide) The energy states follow from the dispersion relation according to: $E_n(k) = \hbar\omega(k)\left(n+\frac{1}{2}\right)$

As an example, the phonon dispersion of the fcc lattice is shown (slide) for the case of Si:

There are two classifications used to describe phonons: longitudinal / transversal and acoustical / optical. For longitudinal phonons, the displacement of the atoms occurs parallel to the direction of the wave, whereas for transversal phonons this displacement is perpendicular to the wave vector. For acoustic phonons, the atoms inside the unit cell move all in the same direction, whereas for optical phonons, these atoms vibrate against each other. When the charges in a crystal are not evenly distributed (e.g. in an ionic crystal), an optical phonon induces an oscillating dipole moment, which allows coupling of these optical phonons to photons. As light is a transversal wave, only coupling to transversal phonons is possible. We have encountered these phonons already in the last chapter as the vibrational oscillators in the Lorentz-model.

A possible way to describe this interaction is in the quasiparticle picture. Here, momentum and energy have to be conserved during absorption of a photon by a phonon. The comparison of the dispersion relation of phonons and photons [slide] show, that this is only possible for the optical branch of the phonon dispersion curve.

We will now turn to the basics of inelastic scattering, which is a means to detect quasi-particles. To start general, we do not yet specify wether the scattered particle is a photon, electron, or neutron. Let us look at the conservation laws for scattering [is like].

First, we have conservation of momentum. Here, we have to remember that due to the broken translational symmetry of space induced by the crystal, momentum is only conserved up to additions of reciprocal lattice vectors.

We have: $\vec{Q} = \vec{q} + \vec{G} = \vec{k} - \vec{k}'$

- $\vec{Q}$: momentum transfer
- $\vec{q}$: momentum of phonon
- $\vec{G}$: reciprocal lattice vector
- $\vec{k}$, $\vec{k}'$: incident and scattered wave

In addition, we have conservation of energy:

$$E = E' + E_{Phonon},$$

which can be used to calculate E_{Phonon}.

For the case of electrons or neutrons, we have $E = \frac{\hbar^2 k^2}{2m}$ and hence

$$E_{Phonon} = \hbar\omega_{Ph} = \frac{\hbar^2}{2m}(k^2 - k'^2).$$

For photons, we have:

$$E_{Phonon} = \hbar\omega_{Ph} = \hbar(\omega - \omega').$$

Furthermore, spin is conserved.

Let us now look at scattering of photons, which is known as Raman scattering around (slide) the visible part of the spectrum. These photons have a very small wave vector:

$$k_0 = \frac{2\pi}{\lambda} \approx \frac{2\pi}{4000\,\text{Å}} \approx 1 \cdot 10^{-3}\,\text{Å}^{-1}$$

The edge of the Brillouin zone (= maximum wave vector of the phonon) is found at

$$\frac{\pi}{a} = \frac{\pi}{2\,\text{Å}} \approx 1{,}5\,\text{Å}^{-1}.$$

We have for visible light is only sensitive to phonons at the very center of the Brillouin zone. Raman spectroscopy can also detect other quasi particles, as the plasmon encountered in the previous chapter.

The schmatic setup is shown in the (slide). As a monochromatic source of high intensity is needed (Raman scattering has a low probability as compared to elastic - Rayleigh-scattering) the laser is the right choice. The very large elastic signal is then filtered and the remaining light is analyzed in a spectrometer.

The atomic process in Raman scattering can also be visualized in an energy level scheme (slide) using virtual energy levels. Besides the creation of a phonon (Stokes process), an existing photon can also be absorbed by the photon (Anti-Stokes).

Anti-Stokes scattering will only be possible if there are phonons present in the material before the light is incident. The probability for anti-Stokes scattering therefore decreases on lowering the temperature as the phonon population decreases. On the other hand, Stokes scattering does not require a phonon to be present and can therefore occur at any temperature. As the population of a given phonon level follows a Boltzmann distribution, the ratio of anti-Stokes to Stokes scattering events is given by:

$$\frac{I_{\text{anti-Stokes}}}{I_{\text{Stokes}}} = e^{-\hbar\omega_{ph}/k_B T}$$ 1 slide

Inelastic light scattering is a weak process. This is because we are dealing with a higher-order interaction than for linear interactions such as absorption. As a example the 1 slide shows a Raman spectrum of GaAs, where the TO and LO phonon are visible. In addition, a weaker peak due to the plasmon occurs.

Recently, Raman spectroscopy was extensively applied to the new material graphene, as it allows (i) to distinguish single-, bi-, and few layer graphene and (ii) allows to asses the quality (defect density) 5 slide.

A Raman microscope can be used to spatially resolve the vibrational properties of the sample, see the slide for a example.

For excitations very close to the Γ-point, the dispersion of these modes can be detected by Raman spectroscopy. This reveals coupling between different modes: The slide shows how the photon and the TO phonon form a polariton in GaP, leading to avoided crossing (anticrossing). Generally, a polariton is a coupling between a photon and a phonon / plasmon / exciton

The spatial resolution can be enhanced even further by performing Raman spectroscopy inside an STM or AFM: Tip-enhanced Raman Spectroscopy (TERS). The basic effect is that the local electric field can be enhanced in a gap between the surface and a metallic tip of the right shape and material (slide). The main Raman signal thus comes from the small area underneath the tip and can be related to the topography measured simultaneously. Here, vibrations of single molecules can be detected, e.g. RNA slide

In optical measurements only phonons at the center of the Brillouin zone ($\vec{q}=0$) can be studied, since energy and momentum conservation can be satisfied only here on account of the great disparity between phonon and photon propagation velocities. The situation is different for neutrons. The 1slide used to illustrate this was already shown in the context of diffraction. It shows the dispersion relation for photons, neutrons and electrons (and He). The region where the phonons live is the intersection of the blue bars (wavelength on the order of interatomic distances, energy in the range of thermal excitations). Of course, $\lambda = \frac{2\pi}{k}$. Only neutrons have the right energy and momentum to map the whole Brillouin zone easily. Therefore, they are the ideal probe to detect phonons.
The experimental setup used here is the triple-axis-spectrometer 1slide. A white beam of neutrons is produced in a reactor and monochromatized using Bragg reflection. The wavelength of the incoming light is then selected by turning the monochromator around the first axis. The orientation of the sample with respect to the beam is altered using the second axis. After the scattering event, the (now reduced) energy of the neutrons is measured

using again Bragg reflection around the ΔL/Δ axis. Variation of incident energy, final energy, scattering angle and sample orientation allows to map the whole Brillouin zone. The (slide) shows an example.

Due to their sensitivity to the magnetic moment, inelastic neutrons are also the right probe for the detection of spin waves or magnons (slide). These are collective excitations of the electrons' spin structure in a lattice. The [slide] shows an example of a measured magnon dispersion curve.

The last method we will discuss is inelastic scattering of electrons, called electron energy loss spectroscopy. Often, an instrument we already encountered, namely the TEM, is used to detect these signals. Although electrons with the right wavelength (or momentum) have rather high energies as compared with photons, electrons can be detected with a very good energy resolution making EELS a feasible method. The setup of a TEM with EELS is shown in the [slide]. The example [slide] shows that one can obtain the same information from EELS as from optical methods.
The ultimate energy resolution is reached in HREELS (high-resolution electron energy loss spectroscopy). Here, losses of a small fraction of an eV can be detected, because the technique allows to resolve small separations between the elastic peak and the loss features. The setup (slide) consists of a cathode system, a first energy dispersive element (a monochromator), a lens system between the monochromator and the sample, a second lens system between the sample and the analyzer, a further dispersive element (an analyzer) and finally the electron detector. One or

two sequential 127° angle cylindrical sector deflectors fixed at constant pass energy are used as a monochromator. From the broad Maxwell distribution of hot electrons emitted by the cathode, it selects electrons in a narrow energy window (typically 1-10 meV and down to a fraction of a meV in the most advanced systems). The analyzer works in a similar way. A channeltron multiplier is a conventional electron detector. The instrument is very surface sensitive. The example (slide) shows the determination of the full phonon dispersion for graphene.

Magnetism

In this chapter we will deal with experimental techniques used to measure the magnetic properties of matter. Let us start with a review of the basic properties of magnetically ordered states. The magnetic interactions between the individual moments can produce different types of magnetic ground states, some of which are illustrated on the slide. These include ferromagnets in which all the magnetic moments are in parallel alignment, antiferromagnets in which adjacent magnetic moments lie in anti-parallel alignment, spiral and helical structures in which the direction of the magnetic moment precesses around a cone or a circle as one moves from one site to the next, and spin glasses in which the magnetic moments lie in frozen random arrangements.

Ferromagnetism

A ferromagnet has a spontaneous magnetization even in the absence of an applied field. All the magnetic moments lie along a single unique direction. This effect is generally due to exchange interactions (direct exchange, super exchange, RKKY). For a ferromagnet in an applied magnetic field $\vec{B}$, the appropriate Hamiltonian to solve is:

$$H = -\sum_{ij} J_{ij} \vec{S}_i \cdot \vec{S}_j + g\mu_B \sum_j \vec{S}_j \vec{B}$$

J_{ij}: coupling constant between i and j; $\vec{S}_i, \vec{S}_j$: spins at positions i and j; g: g-factor (Landé); μ_B: Bohr magneton

The exchange constants J_{ij} for nearest neighbours have to be positive to ensure ferromagnetic alignment. The first term on the right is the Heisenberg exchange energy, the second term is the Zeeman energy.

The ferromagnetic order evolves spontaneously. The degree of ordering depends on temperature and disappears above the Curie-temperature. The typical magnetization vs temperature curves resulting from the mean-field model (Weiss model) are shown in the slide. Note that the disappearance of M above T_c is a second order phase transition.

Antiferromagnetism

If the exchange interaction is negative ($J < 0$), the molecular field is oriented such that it is favorable for nearest neighbour magnetic moments to lie antiparallel to each other. This is antiferromagnetism. Antiferromagnetic order disappears above the Néel-temperature.

Susceptibility

The magnetic susceptibility is defined

as $\vec{M} = \chi \vec{H}$. From the Weiss model of magnetism it follows that:

Ferromagnet: $\chi \sim \frac{1}{T - T_C}$ (Curie-Weiss law) $(T \geq T_C)$

Antiferromagnet: $\chi \sim \frac{1}{T + T_N}$

This can be generalized by defining the Weiss temperature Θ leading to

$$\chi \sim \frac{1}{T - \Theta}$$

For a paramagnet, $\Theta = 0$, for a ferromagnet $\Theta = T_C$, and for an antiferromagnet $\Theta = -T_N$. See the slide for a graphical representation. Measuring the dependence of χ on T is therefore an experimental pathway to determine the kind of magnetic ordering and its parameters. For an antiferromagnet, the behaviour of χ also depends on the geometry of the experiment. slide

For a ferromagnet, the formation of magnetic domains leads to the occurrence of hysteresis loops in the $M(H)$ curves (slide).

Experiments

The most obvious experimental technique to try is a conventional measurement of magnetization, i.e. determine the sample's net magnetic moment. This is done using a magnetometer. This is of course only meaningful with samples having a non-zero magnetization. To have a high signal, special constructions are in use. The first to be discussed here is the vibrating sample magnetometer (VSM). The sample is put into a uniform magnetic field in order to magnetize it. The sample is then vibrating sinusoidially, typically by using a piezo-motor. The changing magnetic field nearby the sample induces a voltage in the pick-up coils: $U_{ind} = -N\dot{\Phi} \sim NV\dot{x}$. Typically, the induced signal is detected using a lock-in amplifier taking the mechanical oscillation as a reference signal. By measuring M as a function of an external field B or as a function of T, hysteresis curves and magnetization curves can be recorded.

slide

The most sensitive magnetometers are using SQUIDs (superconducting quantum interference devices) as sensors. These are formed by a ring of superconducting material (slide). As the flux through such a ring is quantized in units of $\frac{h}{2e}$.

→ also $\chi(T)$

When the external magnetic field is such that in principle a non-integer number of flux quanta has to pass through the loop, a super current is induced which exactly compensates the extra flux. This super current can be read out as a voltage in a ring containing two Josephson junctions. For a typical size of a SQUID, changes in the magnetic field of down to 10^{-15} T can be detected, making the SQUID one of the most sensitive detectors available. In practice, many applications exist where the quantity of interest is first turned in a magnetic signal and then measured using a SQUID

Example: EuO [slide]

Magnetooptics

In order to understand how magnetism can change the interaction of light with media, we have to take a look at the behavior of circular polarized light. For chiral objects the response towards left- and right-circular light will be different. (A chiral object is a object that can not be superimposed with its mirror image like the right and the left hand). A difference in the real part of the complex refractive index gives rise to optical activity while a difference in the imaginary part cause circular dichroism. Optical activity means that the speed of propagation is different for left- and right-circular light and has as a consequence, that the plane of polarization of linear polarized light is turned when light shines through a material with optical activity. Circular dichroism is observed in absorbing chiral materials. "Dichroic" means two-colored and is used for any optical phenomenon that affects two colors differently. In the case of circular dichroism, the absorption coefficient is sensitive to the direction of the circular polarization, which implies that if the absorption bands lie in the visible spectral region, the color will be different when viewed with left- or right-circular light.

Optical chirality can be induced by a chiral crystal structure or in non-chiral material by applying a magnetic field. This induces a number of magneto-optical phenomena. In the case of transparent materials, the field induces optical activity and the phenomenon is called either the Faraday-effect or the magneto-optical Kerr effect, depending on whether the rotation of the polarization is observed in transmission or reflection, respectively. [slide]
If the medium is absorbing, the field can induce circular dichroism, in which case we have magnetic circular dichroism.
Let us first look at the detection of the magneto-optical Kerr effect (MOKE). (slide). As a light-source, typically a laser is used. The light is polarized and focused on the sample. After reflection, the (now changed) polarization is measured. As the amount of the Kerr-Rotation depends on the magnetization of the sample, this technique can be used for the measurement of hysteresis loops (slide).
This technique can also be used to obtain images by forming an image of the sample in polarisation contrast (MOKE microscope) [slide]
By this technique, the distribution of magnetic domains can be imaged (slide).

As an example for magnetic circular dichroism, we will take a look at XMCD (x-ray magnetic circular dichroism). This technique is closely related to x-ray absorption spectroscopy discussed earlier. It has the advantages that it can distinguish the magnetic contributions from different elements and that it is very sensitive. XMCD is the difference for a magnetic material between the absorption of left and right circular polarized x-rays. (Slide) In x-ray absorption, the atom absorbs a photon, giving rise to the transition of a core electron to an empty state above the Fermi level. The absorption edges have energies which are characteristic for each element. Due to the dipole selection rules for the absorption of a photon, the intensities of the absorption lines differ for the two polarizations in the presence of a magnetic field. Using the appropriate sum rules the magnetic moment per atom can be determined and one can even distinguish between orbital and spin momentum. (Slide). As this technique needs a tunable x-ray, it can only be carried out at a synchrotron.

Techniques based on the detection of electrons (LEEM, photoemission) can be turned into methods sensitive to magnetism by measuring the spin of the detected electrons. A device used to detect the spin is the Mott-detector (Mott-polarimeter). This device is based on the spin dependence of the scattering cross section for electrons with atoms. As the scatterer, an atom with a high nuclear charge is used (e.g. gold). The scattering electron penetrates deep into the Coulomb field of the atom. In the rest frame of the electron, the atom moves towards the electron (slide). When the electron is inside the atom, the atomic charge is dominated by the positive nuclear charge. In the rest frame of the electron, the moving electric field generates a magnetic field with circular field lines. The magnetic field is inhomogeneous, it becomes weaker as the distance to the atomic nucleus increases. The large magnetic field gradient exercizes a sizeable force on the magnetic moment of the electron. This force is superimposed onto the Coulomb force acting on the charge of the electron. If the magnetic moment is up and if the electron passes on the right side of the atom, magnetic field and magnetic moment are parallel and the force pushes the electron towards

increasing field, i.e. to the left. If the electron passes on the left side of the atom, magnetic field and magnetic moment are antiparallel and the force pushs the electron towards the weaker field, i.e. to the left as well. Altogether, an electron with magnetic moment up wrt the scattering plane is preferentially scattered to the left, and an electron with magnetic moment down is preferentially scattered to the right. By detecting the intensities of the electron beam on both sides after the scattering, the spin direction can be determined [slide].
The next [slide] shows a setup for spin-resolved ARPES. First, the photoelectrons are sorted according to energy and angle as we have learned before. In an additional step, the 3D orientation of the spin is detected using two Mott polarimeters. The [slide] shows as an example the spin resolved Fermi surface of Ni.

Magnetic resonance techniques

The next techniques we will discuss are able to determine the response of an individual magnetic moment to the local environment it is sitting in. This environment is determined by the crystal field, spin-orbit coupling, and hyperfine interactions (see below). The experimental technique is based on resonant transitions between Zeeman-split states.

Nuclear magnetic resonance (NMR)

For an NMR experiment, one needs a nucleus with a non-zero spin (^1H, ^2H, ^{13}C). In a simple NMR experiment [slide], a sample is placed inside a coil which is mounted between the pole pieces of a magnet. The magnet produces a magnetic field $\vec{B}$, along the z-direction. The z-component m_I of the angular momentum of the nucleus I can only take integral values between $-I$ and I. The energy E of the nucleus with magnetic moment $\vec{\mu}$ in the field $\vec{B}_0$ is then:

$$E = -\vec{\mu}\,\vec{B}_0 \qquad \text{(nuclear magneton)}$$

$$= -g_N \mu_N m_I B_0$$

(g-factor of nucleus)

This corresponds to a ladder of $2I+1$ equally spaced energy levels with a

mutual separation of $g_N \mu_N B_0$ as illustrated in the Isliche for the case $I = 3/2$. For usual fields in the range of 1 T the energy separation corresponds to photons in the radio frequency regime. Therefore, transitions between adjacent pairs of levels can be excited by a radio frequency (RF) field, which is the basis of NMR. In the sketch of the NMR setup, this RF field is provided by the coil around the sample. Only transitions where the dipole selection rule $\boxed{\Delta m_I = \pm 1}$ is obeyed are possible, which implies that only transitions between adjacent states may occur.

In the most common experimental setup, the RF coil is part of a tuned circuit with a large Q factor. The (quasi-) static field B_0 is ramped up, and when the energy separation matches the frequency of the loop, energy is lost which yields the measurable signal (at the position of nuclear magnetic resonance). The resonance frequency is given by

$$\nu = \frac{\omega}{2\pi} = \frac{\Delta E}{2\pi\hbar} = \frac{g_N \mu_N B_0}{2\pi\hbar}$$

The NMR frequency can be slightly shifted depending on the chemical environment of the nucleus (chemical shift), as the

electrons orbiting the nucleus slightly shield it from the applied field. (This chemical sensitivity is the reason for the application of NMR in medical imaging). It can be also changed by nuclear spin-spin coupling mediated by the electrons, therefore containing information about the magnetic environment of the nucleus.

Electron spin resonance

One can perform the analogous experiment to NMR with electrons (electron spin resonance - ESR). As the magnetic moment of the electron is higher than the one of the nucleus, the resonance for typical magnetic fields is in the microwave regime. The technique is therefore based on waveguides and cavities [slide]. Again, the behaviour of the microwave circuit changes significantly when it is operated at a resonance frequency of the sample. ESR allows to detect the local crystal field. This will be explained using an atom in an octahedral environment, a situation found for the metal ion in a perowskite, which is the crystal structure of many transition metal oxides [slide]. The crystal field in this case arises mainly from electrostatic repulsion from the negatively charged electrons in the oxygen orbitals. The outermost

orbitals of the metal are the d- orbitals [slide]. Close inspection reveals that the d-orbitals fall in two groups: The t_{2g} - orbitals which point between the axes (d_{xy}, d_{xz}, d_{yz}) and the eg- orbitals which point along these axes (d_{z^2}, $d_{x^2-y^2}$). As the overlap of the eg - orbitals with the oxygens is stronger, they will be shifted up in energy [slide] This is the crystal - field - splitting. The consequence of crystal - field - splitting for the ESR signal is shown on the [slide]: It leads to a splitting of the absorption lines. This can be used to evaluate the strength of the crystal field and the occupation of the d- orbitals

Thermodynamic Properties

In this section we will see how the quantitative determination of thermodynamic properties can give us important information on phase transitions, and especially on magnetic ordering phenomena. The underlying formula is the dependence of the free energy F of a system on the variables T, B, and V:

$$dF = -S\,dT - m\,dB - p\,dV$$

(m: magnetic moment)

(this is derived from the first law of thermodynamics)

The relation between these quantities is shown on the (slide). As the system always seeks the minimum of F, it can react to changes in one variable by spontaneous changes in the other. In the following we will focus on thermal expansion (changing the temperature changes the volume), magnetostriction (changing the magnetic field changes the volume), and heat capacity (chging the temperature changes the entropy). We will start with looking at experimental methods to determine changes in length of samples

Dilatometry

A dilatometer is a scientific instrument that measures volume changes induced by physical or chemical processes. Historically, the thermal expansion of solids has been studied from the beginning

of material science, see (slide) for an old dilatometer. In the following, we will see that the precise determination of this effect allows to learn much more than just "rails become longer in summer". In principle, several methods we have studied so far allow for a determination of thermal expansion, for example a determination of the structural parameters by x-ray or neutron diffraction. However, much more powerful methods are available (slide). We will now focus on the <u>capacitive dilatometer</u> (slide). The principle of operation is that the expansion of the sample moves one plate of a plate capacitor. Assuming circular plates with radius r, the capacitance is given by:

$$C = \varepsilon_0 \frac{\pi r^2}{d}$$

The change in length is then related to the change in capacitance as:

$$\Delta L = \varepsilon_0 \pi r^2 \left(\frac{1}{c_1} - \frac{1}{c_2} \right)$$

One can reach a resolution in the range of 10^{-10} m. An example for such an instrument is shown on the (slide). A typical sample environment for this kind of measurements are low temperatures (a few K) and high magnetic fields (several T).

<u>Calorimetry</u>

Specific heat is measured with a <u>calorimeter</u>, see (slide) for a historic example. In such an <u>ice calorimeter</u>, the heat transferred from a body

at given starting temperature T_1 to a bath at temperature T_0 is measured by the ammount of ice that can be melted with it. The same principle is used today. The basic ingredients are a temperature bath at given (low) T_0, a heater to transfer energy to the sample, and a precise determination of sample temperature. The actual measurement can be carried out in different ways, as we will see in the following

Nernst method (heat pulse method)

This is probably the most intuitive technique: A sample is thermally isolated from the environment as good as possible (adiabatic conditions). A defined ammount of heat ΔQ is introduced by the heater and the resulting increase in sample temperature is measured (slide). In a sense, this is a direct realization of the definition of C: $C(T) = \lim_{\Delta T \to 0} \frac{Q}{\Delta T}$.

In practice, conditions close to adiabatic are difficult to realize.

Continuous heating method

This procedure is closely related to the Nernst method. Here, the sample is heated continuously under adiabatic conditions, and the heat capacitance is determined as the derivative of the resulting $T(Q)$ curve (slide). This method is less accurate as the Nernst-method, but allows a fast determination with a high density of data points

In the following two methods, the sample is in (weak) thermal contact to the bath. The principle of measurement is based on the fact, that the specific heat determines, how fast the temperature of the sample can react to external heating

Relaxation time method

Here, the sample is heated, until a new equilibrium temperature following the competition between heating and cooling (via the external bath) has been established. Analysing both this rise in T as well as the drop back to T_0 allows a determination of c. (slide)

AC-method

In this approach, the sample is heated using a periodically varying heating power $P(\omega) = I_H \cdot U_H$. The sample reacts with a periodically varying temperature with amplitude ΔT. It can be shown that $c(T) = \frac{I_H \cdot U_H}{\omega \cdot \Delta T}$

Example

To get started with an example, we look at the internal energy of a ferromagnet with $S = 1/2$ and $T_C = 10\,K$. Using mean field theory, it can be shown that the magnetic contribution to the internal energy is:

$$U^{mag} = -N \int B_{eff}\, dM$$

$$= -N \left(\frac{3 k_B T_C S}{2(S+1)} \frac{M^2}{M_{sat}^2} + MB \right)$$

The behavior of $M(T)$ in this example is shown on the slide. In the absence of an external magnetic field B, U^{mag} is zero above T_c and becomes more and more negative the lower we go in temperature. Right at T_c, $\frac{dU^{mag}}{dT}$ has a discontinuity. This discontinuity should show up both in $c = \frac{\partial Q}{\partial T}$ as well as in $\beta = \frac{1}{V_0}\frac{\partial V}{\partial \pi}$. Experimental results for the model compound EuC_2 ($S = 7/2$, $T_c = 14K$) are shown on the slide. An difficulty in the evaluation is to remove other contributions to β and c (phonons).

Creation of low temperatures

Many properties of solids (e.g. magnetic ordering phenomena) can only be studied at very low temperatures (slide). In the following, we will learn how these conditions can be created in the lab. The temperatures that can technically be reached today (10^{-6} K) are several orders below the lowest temperatures occuring in our universe (2.73 K background radiation). One can say that the creation of ultra-low temperatures is one of the few parameters where mankind has surpassed nature. The history of this technical development is shown on the (slide). The methods dominating the refrigeration technique today are shown in the (slide). Properties of matter that can only be studied at very low temperatures include the quantization of lattice vibrations (phonons), the electronic excitations leading to the linear temperature dependence of the specific heat of conduction electrons, superconductivity, superfluidity, and many aspects of magnetism.

Cryoliquids

Bringing the sample into contact with a reservoir containing a cryoliquid (LN_2 - 77K/ L^4He - 4K) is the easiest method of refrigeration. Although today the supply of cryogenic liquids is a routine process, it is instructive to look briefly into the effects underlying gas liquefaction.

A general principle is for cooling is causing a gas to perform adiabatic external work. During this, it must cool due to the first law of thermodynamics. What happens is that some of the internal energy of the gas (the kinetic energy of the molecules) is used to perform the work. There are several ways how to achieve this technically, we will only look at an idealized version of the process, namely a Stirling engine operated in reverse (slide). Two piston and cylinders are used, one at the high temperature T_H, the other at the low temperature T_C. They are connected via a regenerator, a device which has low thermal conductivity, a small internal volume, and a low flow impedance for gas, but a large heat capacity and a large internal surface area (e.g. a tube filled with fine Cu-wire). We assume that the top of the regenerator is at T_H, whereas its bottom is at T_L. In step (a) [A→B] the upper piston moves and compresses the gas at the hot end, while the lower piston stands still. Work is done on the gas and the heat Q_H has to be removed in order to keep T_H constant. In (b) [B→C] both pistons move together to transfer gas from the hot to the cold side. Because of the large heat capacity of the regenerator, the gas is already at T_C when it enters the lower chamber. In c [C→D] the lower piston lets the gas expand.

Work is being done by the gas, which has to be supplied by the environment as heat Q_c. This is the cooling step. In the last step (d) [D → A] the system is brought back to the starting conditions, picking up the heat from the regenerator that has been stored there before.
Remember that the total amount of work is the area enclosed by the path in the p-V-diagram. In our process, the work is taken from the thermal energy of the cold side.
A technique of high technical importance is Joule-Kelvin expansion. Here, gas is allowed to expand through a porous plug (slide). It can be shown that during such a process the enthalpy stays constant, we therefore have to look at the isenthalps (lines of constant enthalpy) in the figure. We see that in a specific regime of the plot, the reduction in pressure due to the orifice is accompagnied by a reduction in temperature. This can only happen if the gas (a real gas) was in a state where the intermolecular interaction is attractive before the plug. The expansion then increases the potential energy, and the kinetic energy (and hence the temperature) go down. As a consequence, this process is only possible in a specific regime in the p-T diagram. However, for most gases this regime is easy to reach

In practice, one can use the cooled gas streaming out to pre-cool the gas streaming in (slide). Thereby, after some time, liquefaction can be reached.

Technologically important processes (Linde process) combine several techniques. It is interesting to note that the liquefaction of air is the common procedure to separate air into its constituencies.

^3He - ^4He Dilution Refrigerator

In order to go below the temperature limit that can be employed by the use of cryoliquids (0.23 K using liquid ^3He), the device most commonly used today is the ^3He-^4He dilution refrigerator. This device is based on a process suggested in 1962 by London, Clarke, and Mendoza. In contrast to using the latent heat of evaporation for cooling, here the heat of mixing of the two He isotopes is used to reach low temperatures. In order to understand this device, we have to take a look at the properties of liquid ^3He-^4He mixtures. The (slide) depicts the x-T phase diagram of such a mixture at saturated vapor pressure. (x is the relative concentration of ^4He). The superfluidity (fluid with zero viscosity) of ^4He due to its bosonic nature is depressed by diluting it with the fermionic ^3He. The shaded region under the phase-separation line is a non-accessible range of temperatures and concentrations

for helium mixtures. If we cool an appropriate mixture to below 0.87 K, the liquid will phase separate in a ^4He-rich and a ^3He-rich phase. Upon reaching 0 K, we have on the one side pure ^3He, but on the other side a mixture containing 6,6% ^3He in ^4He. This finite solubility at 0 K is an exceptional behaviour and of utmost importance in ^3He-^4He dilute refrigeration technology. As we will se below, cooling in a ^3He-^4He dilution refrigerator is achieved by transferring ^3He atoms from the pure ^3He phase to the diluted, mostly ^4He containing phase. The cooling capacity in this case is the heat of mixing. In general, if the intermolecular forces between A and B are larger than the ones in A-A and B-B, the potential energy upon mixing rises. This is compensated by a loss in kinetic energy, i.e. temperature.

The isotope ^4He in the mixture has a nuclear spin $I=0$ and therefore in its liquid state it obeys Bose statistics and undergoes a Bose condensation into the superfluid state at low-enough temperature. This means that the liquid is in a quantum-mechanical ground state, containing essentially no excitations (phonons). Its viscosity, entropy, and specific heat go to zero. In a helium mixture at sufficiently low T, the component ^4He acts as a kind of inert superfluid

background which contributes to the volume of the liquid and to the effective mass of the dissolved ^3He, but has negligible heat capacitance. ^3He, on the other hand has nuclear spin $I = 1/2$ and is a Fermion, i.e. it obeys Fermi statistics and the Pauli exclusion principle. Its Fermi temperature is very low ($\approx 1K$), which means that it behaves like a classic gas above 1K, but as a Fermi gas significantly below this temperature. The effects of diluting ^3He in ^4He can be taken into account as a changed Fermi temperature and changed effective mass. The ^3He atom needs more space than ^4He due to its larger zero-point motion (smaller mass). Hence, when a single ^3He is put into ^4He, it is closer to neighboring atoms than it would be in pure ^3He, and it has more potential (van-der-Waals) energy. As a consequence, energy is gained by moving ^3He to ^4He. However, due to Pauli repulsion, this effect is over compensated for a specific concentration. This explains the finite solubility of ^3He in ^4He. The stronger binding of ^3He in ^4He leads to lower kinetic energy, i.e., a reduction in temperature. Note that this considerations would also hold without the finite solubility at 0K. However, for $x \to 1$ at $T \to 0$, the process would become very inefficient, which is not the case in the real system

The enthalpy of mixing is used as the cooling step in a ^3He-^4He dilution refrigerator. The schematic setup is shown in the slide. Let us follow the flow of ^3He through the device: ^3He gas coming from the exit of a pump at room temperature is first precooled by a liquid ^4He bath at 4.2 K. It will then be condensed to liquid ^3He in a second ^4He bath at 1.5 K, which can be reached by pumping on liquid ^4He. Special care has to be taken in the design of the precooling and condensing unit to allow for efficient heat transfer. The liquid ^3He will flow through a heat exchanger which is in thermal contact with (or even inside) the still at a temperature of about 0.7 K. After this, the liquid ^3He will flow through a series of heat exchangers to precool it as much as possible before it enters the upper, concentrated phase in the mixing chamber. This additional amount of ^3He in the mixture has to be distributed according to the phase diagram shown above. In consequence, the largest part stays in the concentrated phase, but a significant fraction crosses the phase boundary and extracts heat from the surroundings due to the enthalpy of mixing. Because of the finite solubility of ^3He in ^4He even at 0 K, this is an efficient process down to the lowest temperatures.

The dilute phase in the mixing chamber is connected to the almost pure ^4He in the still. The different concentrations lead to an osmotic pressure: ^3He wants to travel up in order to reach an equilibrium in the concentrations. One can calculate that the osmotic pressure is high enough to lift the ^3He by 1 m. After passing the heat exchangers in opposite direction, the ^3He enters the strongly diluted phase in the still. The vapor above the diluted phase, however, is almost pure ^3He due to its significantly higher vapor pressure compared with ^4He. This vapor is pumped away by our pumping system, and behind the pump the cycle can start again. A schematic drawing of a real setup is shown in the (slide).