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MAGNETO-OPTICAL MICROWAVE SPECTROSCOPY OF THE COHERENT MAGNETIC STATE IN THE MIXED VALANCE COMPOUND SmB_6 IN THE FREQUENCY RANGE 40–120 GHz

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In undoped pure single crystals of the mixed valance compound SmB_6 anomalous ESR absorption has been observed in the frequency range $\nu = 40 - 120$ GHz at temperatures of 1.8 – 4.2 K. The ESR for the case of the coherent ground state consists of two components corresponding to g-factors $g_1 = 1.907 \pm 0.003$ and $g_2 = 1.890 \pm 0.003$. The amplitude of both ESR lines strongly depends on temperature in the temperature range studied: the amplitude of the first line with $g = g_1$ increases and the amplitude of the second line decreases with temperature. A model based on consideration of the intrinsic defects in the SmB_6 crystalline lattice having concentration $\sim 10^{15} - 10^{16}$ cm^{-3} is suggested for the explanation of the anomalous ESR-behaviour. In the frequency range $\nu > 70$ GHz at $T = 4.2$ K, in addition to the main ESR lines, a new magnetic resonance with an hysteresis-like field dependence is discovered.

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1. Samarium hexaboride, SmB_6, is an example of a mixed valance compound [1] whose ground state at low temperatures is characterised by the presence of a correlation gap $\sim 50 - 100$ K at the Fermi level [2]. However the nature of the coherent state in SmB_6 remains the subject of debate, even though the first investigations into the properties of this compound have appeared more than thirty years ago (see Ref. [3] and the literature cited therein). Probably the most adequate description of the phenomenon is the Kondo-insulator model [4], which takes into account the magnetic interactions of Sm^{3+} ions and screening due to free carriers [4].

The experimental study of the low-frequency optical and magneto-optical properties of this material is rather incomplete. Mainly reflectance spectra in the frequency range $\nu \geq 250$ GHz have been studied in detail [5,6] and there are only a few transmission measurements for $\nu \geq 600$ GHz [7]. At lower frequencies, measurements of the temperature dependence of the microwave conductivity have been performed for $\nu = 9$ GHz [8]. Note that all experiments [5-8] were performed in the absence of a magnetic field.

In a magnetic field, it is necessary to consider the possibility of observing ESR. In the low-temperature coherent state the magnetic moment of samarium is quenched, so in the absence of disorder or magnetic impurities an ESR signal should not be observed. In the majority of studies of ESR in SmB_6, experiments have therefore been carried out on samples doped with Gd^{3+} or Eu^{2+} magnetic ions [9-12]. However, all published ESR studies have been done in the standard ESR range $\nu \leq 40$ GHz, and hence there is a "gap" in the frequency range $40 \leq \nu \leq 250$ GHz, where no experimental magneto-optical data are available.

We have recently shown [13,14] that magneto-optical studies in this particular frequency range can be used to perform effective spectroscopy of Kondo-lattice heavy-fermion compounds. The aim of the present work is the study of the corresponding resonant magnetoabsorption in the case of mixed valance compound. Experiments were done on the pure undoped SmB_6 single crystals in the frequency range $40 \leq \nu \leq 120$ GHz at helium temperatures, i.e. within the coherent ground state.

2. Measurements of the transmission in a magnetic field H up to 70 kOe were performed on a magneto-optical spectrometer which uses BWT-generators with a 10 mW output as sources of microwave radiation. The installation allowed us to carry out experiments at two fixed temperatures $T = 1.8$ K and $T = 4.2$ K. The radiation was transmitted by a waveguide into a cryostat containing a vertical magnet. The sample of SmB_6 was mounted on a thin aluminium diaphragm with a bore diameter somewhat less than the sample diameter ~ 5 mm. In order to avoid radiation leakage, the sample was glued to the diaphragm by conducting silver paint. A miniature carbon bolometer, to detect radiation transmitted through the sample, was located just after the diaphragm. The temperature of the sample was controlled by an independent thermometer mounted on the diaphragm. For better thermal contact and stability, experiments were done in low-pressure helium exchange gas. A detailed description of the experimental installation is given in Ref. [15].

Because the radiation detector, as well as the sample, was subjected to high magnetic field and microwave radiation, it is necessary to eliminate any possible contribution to the measured bolometer signal coming from resonant absorption of microwave radiation in the detector itself. In order to do this, samples of SmB_6 with thickness $d = 2$ mm and $d = 0.5$ mm were studied. Note that for the experimental values of the resistivity ~ 2 Ohm cm at $T \leq 4.2$ K the estimate of the skin-depth gives $\delta = 0.35 - 0.22$ mm for $\nu = 40 - 100$ GHz. Consequently in the case $d = 2$ mm $\gg \delta$, the sample is not transparent and any contribution from the detector can be excluded. In the second case ($d = 0.5$ mm $\sim \delta$) we can estimate the magnitude of the transmission

$$\mathrm{Tr} \sim (e^{-d/\delta})^2 = 6 \ - \ 1 \ \%,$$

which is far above the limit of resolution of our installation Tr $\sim 5 \times 10^{-5}$. So for the thin sample, direct magneto-optical transmission measurements are possible, however the above value of the transmission is 3–5 times overestimated as compared with experimental value $\mathrm{Tr}(H = 0) \sim 1 - 0.3$ %. This result may serve as an indication of the presence of strong non-electronic absorption in SmB_6 and is in agreement with the data reported previously in [7], where a similar discrepancy of up to an order of magnitude was noticed for $\nu \sim 600$ GHz.

3. The typical field dependence of the transmission $\mathrm{Tr}(H)$ at fixed frequency for $T = 4.2$ K are shown on Fig.1. A remarkable feature is the presence of the narrow resonant doublet, S_1 and S_2, located in the region $g \sim 2$. There is also a weaker line X, which demonstrates anomalous behaviour: it was observed only in the magnetic field scans where the field was increased and never on the sweeps down (see Fig.1: a, b – correspond to sweep up and c, d – to sweep down). The

feature marked on fig.1 as line U represents the contribution from the measuring unit deduced as described above.

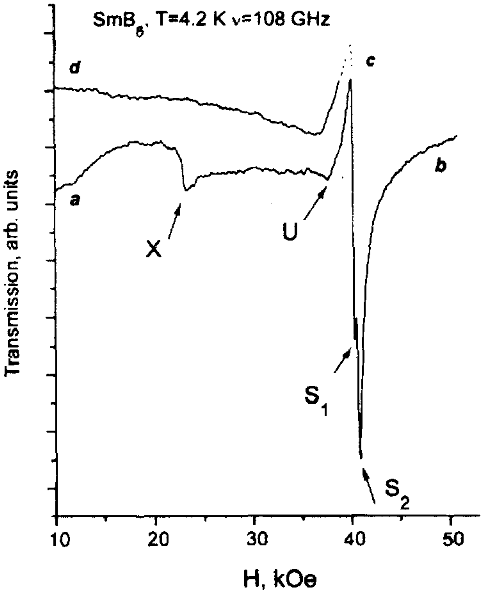

Fig.1. General structure of the transmission signal for pure SmB_6 at 4.2 K for frequency 108 GHz: a, b – corresponds to data with increasing magnetic field, c, d – corresponds to data with decreasing magnetic field

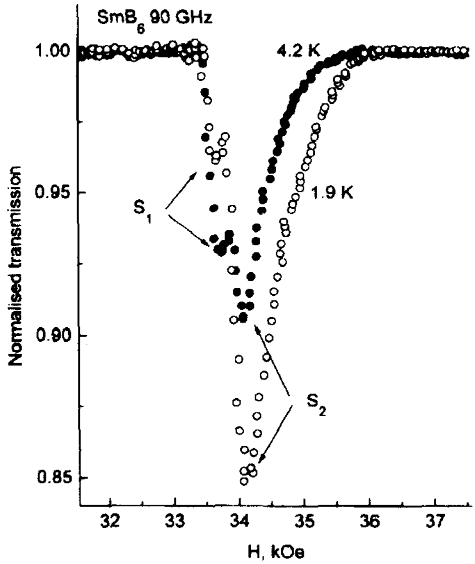

Fig.2. ESR lines in SmB_6 at 4.2 K and 1.8 K. For correct normalisation of the spectra the contribution from the experimental unit was taken into account (see text for details)

The absorption in the vicinity of the main ESR-doublet is strongly temperature dependent (Fig.2). First of all, the amplitude of the line S_2 increases up to ~ 15 % of the level $\mathrm{Tr}(H = 0)$ when the temperature is lowered from 4.2 K to 1.8 K. Secondly for $T = 1.8$ K, a dramatic decrease of the amplitude of the line S_1 is observed: at $T = 4.2$ K the amplitudes of S_1 and S_2 are comparable, but at $T = 1.8$ K the ratio of the amplitudes is about 1:4. At the same time both the positions and widths of the lines do not appear to depend on temperature (Fig.2). The line X was not also observed at $T = 1.8$ K.

The positions of the magnetic resonances observed in SmB_6 are summarized in Fig.3. The slope of the lines $\nu \sim H$ allowed us to calculate g-factor values for the modes S_1 and S_2: $g_1 = 1.907 \pm 0.003$ and $g_2 = 1.890 \pm 0.003$, where the error values were deduced from standard linear regression analysis. Although the measured g-factor values are close to $g = 2$, they are both considerably smaller, which could be indicative of the strong renormalization effects for ESR in pure SmB_6.

Data $\nu(H)$ for the anomalous mode X can be extrapolated to the value $\nu(H = 0) \sim 70$ GHz, i.e. in this case $\nu(H = 0) \neq 0$ (Fig. 3). This behaviour is characteristic for some modes of antiferromagnetic resonance [16] as well as for absorption on impurity centres in which the position or splitting of the ground state depends on the magnetic field.

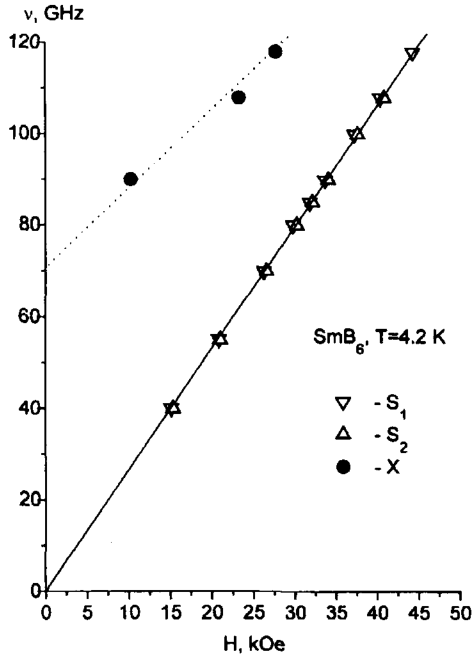

Fig.3. Positions of the various magnetic resonances in SmB_6 at 4.2 K. The resonances are labelled in the same way as on Fig.1

4. The experimental results reported in the previous section are rather unusual. First of all, it is surprising to find a strong absorption in the region $g = 2$ for the coherent state in the undoped case. Note that the previous experiments done at lower frequencies [17] give no indications of such behaviour. Secondly, the strong temperature dependence of the amplitude of the magnetoabsorption lines (Fig.2) for $T \leq 4.2$ K is also unexpected, because in this temperature range the formation of the ground state in SmB_6 would appear to be completed [1, 4]. Thirdly, the presence of the anomalous line X demonstrating strong hysteresis is also difficult to explain in the framework of standard models of mixed valance state for SmB_6. The complete interpretation of the novel features observed in our experiments is the subject of future theoretical and experimental studies and here we will concentrate on the possible nature of the resonant absorption in $g = 2$ region.

The crystal structure of SmB_6 consists of two interpenetrating cubic lattices, one containing Sm atoms and one containing B_6 octahedra. If the Sm or B_6 ions on regular sites exchange their position, the resulting local defect can be considered as an ESR-active impurity [17]. To achieve charge neutrality, the disordered ion Sm^{3+} may capture electrons on the deep $4f$-states and/or weakly trap electrons on external orbitals to form a donor-like state. The capture of electrons will of course change the charge of the Sm ion from Sm^{3+} to one of Sm^{2+},Sm^{+},...,Sm^{3-}, depending on the number of electrons captured. In addition, when analysing ESR it is necessary to take into account the possible coupling of the trapped or captured electrons with spin s according to the $\mathrm{L} + (\mathrm{S} + \mathrm{s})$ model, or coupling with momentum J for the $\mathrm{J} + \mathrm{s}$ model [17].

We wish to emphasise that in contrast to the previously reported results [17], resonances around $g \sim 2$ were observed in the present work, whereas before only resonances with $g \sim 1$ and $g \sim 3-5$ were detected at $\nu \approx 9$ GHz in pure SmB_6 [17].

Let us consider in more detail the possible states of disordered Sm ions which may give rise to g-factors close to 2. According to ref. [17] these states may be $Sm^{3+}(4)$ and Sm^{1+} with $g \approx 2$ as well as $Sm^{3+}(2)$ with $g \approx 1.81$, the latter under the additional assumption of ferromagnetic coupling in the J+s model. The number in brackets corresponds to the number of quasi-donor electrons captured on the external orbitals. In addition to these states the disordered B_6 cluster may also give an ESR signal with $g \approx 2$ [17].

All the states of the disordered Sm ions mentioned above contain a lot of electrons captured on the outer quasi-donor states. Consequently one can expect the effective interactions of these electrons with the magnetically coupled ground state to result in g-factor renormalization (this may be observed experimentally, see previous section).

So on a qualitative level, the model postulating the presence of disordered Sm ions and/or disordered B_6 clusters in the pure SmB_6 matrix [17] can explain many features of the experimental data presented in this work. The doublet structure of the ESR-line may originate from the existence of several types of defects with different electronic configurations. More difficult to account for is the strong temperature dependence observed, but it is reasonable to suppose that some of the disordered states of the Sm ion have energies very close (perhaps ~ 0.1 meV) to that of the ground state, and located in the vicinity of the Fermi-level. In this case the temperature dependence of the components of the doublet would reflect the depopulation of the upper state when the temperature is lowered.

Moreover, considering the data on the absolute values of the transmission (see section 2), we find that for the amplitude of the main line $\sim 0.1-0.15$ which is observed on the level Tr$\sim 0.001-0.01$ it is necessary to change the integral absorption coefficient by approximately 2%. In this case it follows from the standard formula for the ESR-amplitude [18] and the value of the low-temperature magnetic susceptibility ~ 3 emu/mol [19] that the experimental magnitude of the ESR-absorption (Fig.2) can be explained if the defect concentration is in the range $N \sim 10^{15}-10^{16}$ cm^{-3}. This estimate seems to be quite reasonable and hence may serve as an additional argument in favour of the proposed interpretation.

Summarising, in the present work we have studied ESR absorption in pure undoped SmB_6 single crystals by means of magneto-optical transmission measurements for $40 \leq \nu \leq 120$ GHz. We find two lines which contribute to the ESR absorption corresponding to g-factors $g_1 = 1.907$ and $g_2 = 1.890$, and the amplitude of the lines strongly depends on temperature in the interval 1.8–4.2 K. Our results are consistent with a model which considers the intrinsic defects in the crystal lattice of SmB_6, which have concentration $N \sim 10^{15}-10^{16}$ cm^{-3}. The essential deviation of the observed g-factor values from the standard one, $g=2$, may be evidence for strong interactions between the defect and the electrons captured by the defect.

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