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MAGNETIC LOW DIMENSIONAL EFFECTS IN $(Dy_{0.375}Y_{0.625})_2Cu_2O_5$ STUDIED BY ESR SPECTROSCOPY

J. Typek[1] and N. Guskos[1,2]

[1]Institute of Physics, Szczecin University of Technology, Al. Piastow 17, 70-310 Szczecin, Poland
[2]Solid State Section, Department of Physics, University of Athens, 15784 Zografu, Athens, Greece

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Abstract. The powder sample of $(Dy_{0.375}Y_{0.625})_2Cu_2O_5$ solid solution has been synthesized by the solid state reaction method. X-ray characterization showed that the sample is single phase with the following orthorhombic lattice parameters: *a*=1.0817 nm, *b*=0.3502 nm, *c*=1.2462 nm. Electron spin resonance (ESR) measurements of this compound has been carried on a Bruker E500 X-band spectrometer in the 4–300K temperature range. A single Lorentzian-shaped resonance line has been registered with changing integrated intensity, linewidth and resonance field. The integrated intensity of the resonance line showed a pronounced maximum at 21K and vanished at the transition to the antiferromagnetic ordering at T_N=11K. Below 50K, on approach to T_N, the linewidth exhibited a divergent behavior due to the onset of three-dimensional magnetic order. The observed changes of the ESR parameters are interpreted in terms of the low dimensional magnetism of the copper-oxygen system in $(Dy_{0.375}Y_{0.625})_2Cu_2O_5$.

1. INTRODUCTION

$(Dy_{0.375}Y_{0.625})_2Cu_2O_5$ belongs to the family of $R_2Cu_2O_5$ compounds (R=rare earth element smaller than Gd, i.e. Tb, Dy, Ho, Yb, Er, Tm, Lu, as well as Y, Sc, In) with the orthorhombic $Pna2_1$ space group symmetry [1-3]. The most characteristic feature of the $R_2Cu_2O_5$ crystallographic structure is the zigzag copper chains along the *a*-axis. There is a distorted square planar arrangement of four oxygen atoms around copper, with a fifth oxygen making a sort of pyramid. These copper-oxygen pyramids are joined at the common edges into Cu_2O_8 dimers. These dimers, through a bridging oxygen, form an infinite zigzag Cu_2O_5 copper-oxygen chains. Furthermore, each copper is coupled to four other Cu ions along the *b*-axis forming *ab*-pseudoplanes. The rare earth ions are octahedrally coordinated and these distorted RO_6 octahedra are linked in a three-dimensional network occupying the space between copper-oxygen planes [3].

All $R_2Cu_2O_5$ order antiferromagnetically at low temperatures, ranging from 11K (Dy) to 30K (In), and most of them exhibit metamagnetic behavior below Neel temperature [4]. The magnetic properties of $Y_2Cu_2O_5$ have been studied extensively [4-10]. Above 120K, the magnetic susceptibility of this compound is well described by the Curie-Weiss law with a positive Curie temperature, θ=38.5 K, indicating a considerable contribution of ferromagnetic interaction [4]. At T_N=11.5K a sharp maximum in

Corresponding author: J. Typek, e-mail: typjan@ps.pl

the susceptibility gives a strong indication of an antiferromagnetic ordering. In the antiferromagnetic state two jumps in the $M(H)$ magnetization curve (with the external field H applied along b-axis) are observed, corresponding to the two metamagnetic transitions [10]. The magnetic properties of $Dy_2Cu_2O_5$ have been investigated previously [4-6]. The susceptibility follows the Curie-Weiss law exactly down to the transition temperature of T_N=11K, with a negative value of the Curie-Weiss temperature Q=-18K (antiferromagnetic interaction) [4]. The magnetic structure in an ordered state of $R_2Cu_2O_5$ compound could be viewed as consisting of ferromagnetic CuO layers parallel to the *ab*-plane coupled antiferromagnetically with the copper magnetic moments aligned along the *b*-axis. These copper pseudoleyers are bracketed by two Dy layers. Despite a large experimental material gathered from magnetic susceptibility and neutron diffraction measurements the nature of magnetic interactions in the $R_2Cu_2O_5$ family is still incomplete.

Solid solutions of the type $(R_xR'_{1-x})_2Cu_2O_5$ could be prepared by the solid state reaction technique. XRD, termogravimetry, and electron spin resonance (ESR) at room temperatures have been used to study $(Er_xY_{1-x})_2Cu_2O_5$, $(Dy_xY_{1-x})_2Cu_2O_5$, and $(Tb_xY_{1-x})_2Cu_2O_5$ solid solutions [11-13]. Only signal from the copper(II) ions has been registered by conventional X-band ESR spectroscopy. It was found that the relative ESR signal intensity varies with the magnetic rare earth ion concentration index x according to a simple power law function.

The aim of this work is to extend previous room temperature ESR study of $(Dy_{0.375}Y_{0.625})_2Cu_2O_5$ to a wider temperature range, (4-300K), in order to gain insight into the dynamics of copper spin system. Special attention will be paid to the behaviour of copper spin chains present in the $(Dy_{0.375}Y_{0.625})_2Cu_2O_5$ structure in the low temperature range, close to the transition to the antiferromagnetic phase.

2. EXPERIMENTAL

Ceramic sample of $(Dy_{0.375}Y_{0.625})_2Cu_2O_5$ has been prepared by heating in air of an appropriate stoichiometric amounts of metal oxides and was described elsewhere [15]. X-ray characterization showed that the sample is single phase with the following orthorhombic lattice parameters: a=1.0817 nm, b=0.3502 nm, c=1.2462 nm. No significant traces of the copper tetramers in this sample have been observed by ESR spectroscopy.

ESR variable temperature experiments were performed on a Bruker E 500 spectrometer operating at X-band microwave frequency equipped with TE_{102} cavity with 100 kHz field modulation. The investigated sample was in form of loose powder and during the measurements it was placed in a quartz tube. The sample was cooled by flowing He gas and the temperature was controlled within about 1% by using a digital temperature controller. In this paper, the resonance magnetic field B_{res} is defined as the field where the applied magnetic field derivative of the resonance absorption line becomes zero. The effective g-value, g_{eff}, will also be used, defined by the relation $h\nu=g_{eff}\mu_B B_{res}$, where μ_B is Bohr magneton, and ν - the used microwave frequency. Decomposition of the observed ESR spectrum on constituent components has been done by using the SIMPOW computer program.

3. RESULTS AND DISCUSSION

ESR spectra of $(ErY)_2Cu_2O_5$ at selected temperatures are presented in Fig. 1. At a specific temperature, the spectrum is formed by a single, nearly symmetrical, Lorentzian shape line. ESR signal amplitude initially increases as the temperature is decreased from room temperature. Also the linewidth broadens with temperature decrease, especially very quickly in the low temperature range, close to the transition temperature. At the lowest investigated temperatures the ESR line was very broad and asymmetrical. Its amplitude was smaller than at intermediate temperatures, reaching maximum at about 40K. The spectra, although very broad and asymmetrical, were observed down to the temperature of the appearance of an antiferromagnetic state for this sample, i.e. 11.5K. It could be deduced that the registered ESR signal originates only from the copper ions located in the neighbourhood of nonmagnetic Y^{3+} ions and not these close to the magnetic Dy^{3+} ions. This would be consistent with the conclusion made previously that the presence of a magnetic ion effectively switches out the copper ions in its vicinity from taking part in ESR signal formation [11-13].

Fig. 2 presents the temperature dependence of the effective peak-to-peak linewidth, ΔB_{eff}, and the resonance field, B_{res}, in the whole investigated temperature range. In the low temperature range (T<50K), critical behaviour of the ESR parameters (linewidth, g-factor, integrated intensity) due to approach to the antiferromagnetic phase transition, are expected. The sharp increase in the linewidth with decreasing temperature is indicative of cooperative character of the magnetic ordering and can be ex-

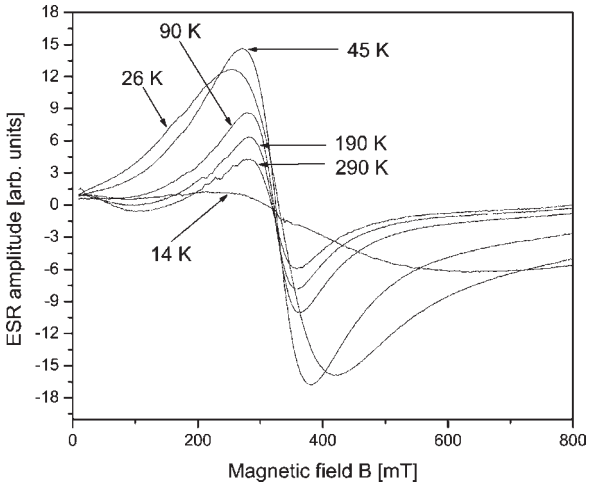

Fig. 1. ESR spectra of $(Dy_{0.375}Y_{0.625})_2Cu_2O_5$ at selected temperatures.

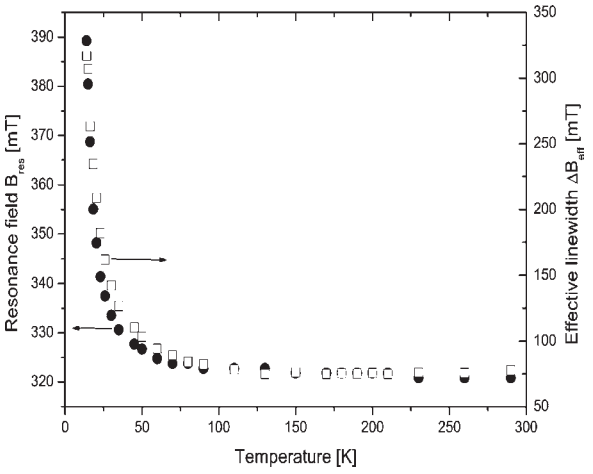

Fig. 2. Temperature dependence of the effective resonance field B_{res} (full circles, left axis) and effective linewidth ΔB_{eff} (empty squares, right axis).

plained by magnetic fluctuations in the vicinity of the transition temperature.

As there are copper(II) (S=1/2) chains present in the crystal structure of $(Dy_{0.375}Y_{0.625})_2Cu_2O_5$ it would be desirable to recall the results of theoretical investigations of ESR spectra of such objects. Oshikawa and Affleck have considered S=1/2 quantum 1D spin chains in the critical region, where the temperature T is sufficiently small compared to the characteristic energy of the exchange interaction J, but T is still large compared to 3D ordering temperature [14]. They also took into consideration the effects of an effective staggered field (staggered g-tensor, Dzialoshinskii-Moriya interaction) that is produced by the applied uniform field and is approximately perpendicular to the applied field. It was found that the staggered field contributes to the linewidth proportionally to h^2/T^2, where h is the magnitude of the staggered field. Thus, the linewidth increases as the square of temperature as the temperature is lowered. As the shift of the resonance frequency (or field) is concerned the theoretical prediction gives the temperature dependence as T^{-3} [14]. Exactly such thermal behavior of linewidth and resonance field was observed for Cu benzoate [15,16].

Fig. 3 presents temperature dependence of the linewidth ΔB_{eff} for $(Dy_{0.375}Y_{0.625})_2Cu_2O_5$ solid solution, demonstrating a linear dependence between ΔB_{eff} and T^{-2} for temperatures below 70K. Fig. 4 shows thermal dependence of the resonance field B_{res}. It is clearly seen that there is a linear dependence between B_{res} and T^{-3} for temperatures below 70K. Thus for both linewidth and resonance field, the theoretical predictions for 1D S=1/2 Heisenberg antiferromagnetic chains are fulfilled by the $(Dy_{0.375}Y_{0.625})_2Cu_2O_5$ compound.

Another important ESR parameter is the integrated intensity, I_{int}, defined as the area under the ESR absorption curve. In the paramagnetic regime I_{int} is proportional to the static susceptibility of spins participating in the resonance. Fig. 5 presents the temperature dependence of I_{int} (upper panel) and the reciprocal of integrated intensity (lower panel). In the intermediate temperature range, 75K<T<200K, a Curie-Weiss type of behaviour, $I_{int}=C/(T-\theta_{CW})$, is observed. Least-squares fitting of the experimental data in that temperature range gave θ_{CW}=26K. Positive sign of the Curie-Weiss temperature evidences ferromagnetic interactions between the copper paramagnetic centres.

A distinct characteristic feature of thermal dependence of I_{int} is a clear maximum observed at T_{max}=21K. The appearance of maximum of the integrated intensity (and thus spin susceptibility) at temperature different than T_N is a clear manifestation of a low dimensional magnetic system. An empirical criterion for determination of the magnetic dimensionality is offered by the ratio T_N/T_{max}, where T_{max} is the temperature of maximum susceptibility [17]. For 1D magnetic systems T_N/T_{max} <0.1, for the 2D systems 0.25<T_N/T_{max} <0.5, and T_N/T_{max} >0.9 for 3D magnets. Applying this criterion to our spin sys-

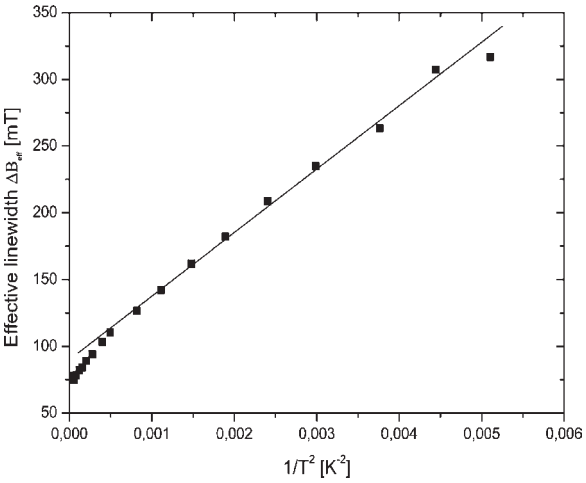

Fig. 3. Temperature dependence of the linewidth ΔB_{eff} demonstrating a linear dependence between ΔB_{eff} and T^{-2} for temperatures below 70K.

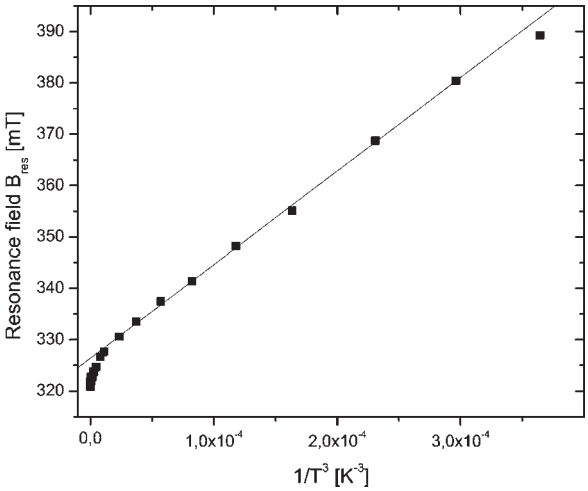

Fig. 4. Temperature dependence of the resonance field B_{res} demonstrating a linear dependence between B_{res} and T^{-3} for temperatures below 70K.

tem (T_N/T_{max}=0.52) it could be concluded that as the integrated intensity is concerned the $(Dy_{0.375}Y_{0.625})_2Cu_2O_5$ solid solution behaves like a 2D magnetic system.

An attempt has been made to fit the measured temperature dependence of integrated intensity by an expression obtained by Bonner and Fisher [18]. They calculated the magnetic susceptibility for a spin S=1/2 1D Heisenberg linear chain. The fitting has not produced satisfactory result, because the measured integrated intensity decreases with temperature increase more abruptly than the theoretical expression. Also the fitting with curves appropriate for Ising 1D model, $I_{int}(T)=(C_1/T)\cdot\exp(-C_2/T)$, or dimer model, $I_{int}(T)=C_3/[T(3+\exp(C_4/T)]$, did not give satisfactory outcome. One of the main reason of fitting failure might be a strong interaction of copper spins with magnetic (Dy) and nonmagnetic (Y) ions, which are statistically distributed at the same crystallographic sites in the $(Dy_{0.375}Y_{0.625})_2Cu_2O_5$ solid solution. This makes the copper chains effectively torn up into many small segments of varying lengths.

Above 200K an increase of the integrated intensity is observed. At the same temperature the

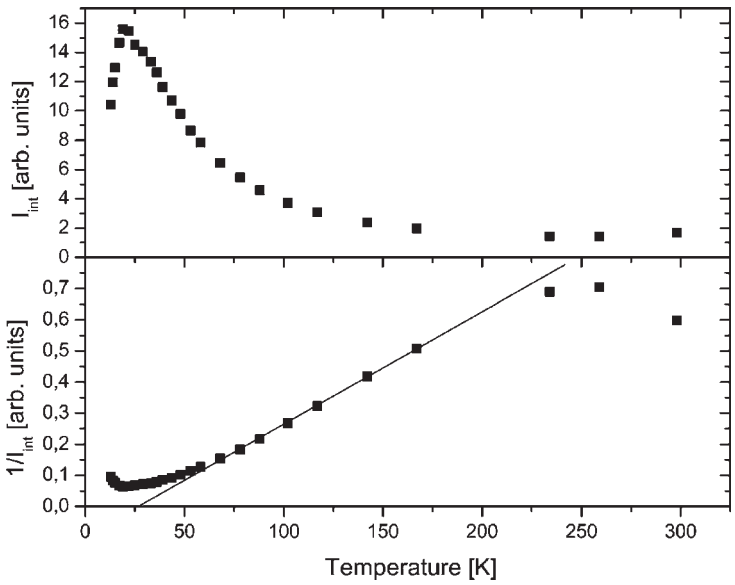

Fig. 5. Temperature dependence of the ESR integrated intensity (upper panel) and reciprocal integrated intensity (lower panel). Solid line is the least-squares fit to the Curie-Weiss law with θ_{CW}=26K.

linewidth reverses its trend of decreasing with the temperature increase and begins to increase (Fig. 2). This increase in thermal dependence of the integrated intensity could be connected with the presence of a small number of isolated copper dimers formed in the –O-Cu-Cu-O-Cu-Cu-O- spin chains. At high enough temperatures, T>400K, the spins are expected to behave as S=1/2. When the short range order develops in this compound as a result of decreasing T, a pair of the two spins which antiferromagnetically couple is expected behave as a spin with S=0. The number of the pairs (each pair could be regarded as a singlet dimer) increases with decreasing T, what is producing a decrease of the integrated intensity, as most dimers fall into non-magnetic S=0 ground state. The dimers are not registered by ESR spectrometer below 200K. The increase of observed linewidth above the same temperature may be the result of existence of an additional relaxation channel (through dimer subsystem) in high temperatures.

ESR of powder samples provides only limited information on the investigated specimens due the availability of only averaged magnetic characteristics. Computer simulation programs might help to resolve the observed powder spectrum into its anisotropic g_i-factors and ΔB_i components. We have used SIMPOW program and were able to make the decomposition of spectra registered at temperatures higher than 70K. The spectra of $(Dy_{0.375}Y_{0.625})_2Cu_2O_5$ at lower temperatures were too anisotropic, probably due to the admixture of non-diagonal terms in dynamic susceptibility [19]. The result of decomposition is presented in Fig. 6. The upper panel in Fig. 6 presents temperature dependence of three DB_i linewidths, while the lower panel of three g_i-factors. As could be easily noticed, already at temperature as high as 150K the g_i-factors starts to differ, and the difference grows rapidly with lowering temperature. Thus one can conclude that the local internal field, produced by local order of copper spins, develops at temperatures much higher than T_N. Unfortunately, decomposition of ESR spectra was not possible close enough to T_N and, particularly, the behaviour of g_i-factors of 1D and 2D systems differs considerably in that temperature range. The g-shifts for parallel and perpendicular orientations should have opposite signs and have a 2-fold difference in magnitude [20].

As could been seen, a rather complicated spin dynamics of the copper system in the $(Dy_{0.375}Y_{0.625})_2Cu_2O_5$ solid solution has been studied by ESR spectroscopy. The obtained results indicate on the presence of low dimensional magnetism in this compound, although not of a typical 1D or 2D conduct. In the low temperature range, close to the T_N, temperature dependence of linewidth and resonance field follows clearly the behaviour expected for S=1/2 AF quantum chains. On the other hand, in the same temperature range, the integrated intensity displayed features characteristic for 2D, and not 1D magnetism. The complications rise probably from the fact that there is a very strong interaction between magnetic copper and dysprosium sublattices in the $(Dy_{0.375}Y_{0.625})_2Cu_2O_5$ and that the ESR signal arises only from copper ions which are close to Y ions and not Dy ions. Taking into account statistical distribution of both rare earth ions it leads to the effective segmentation of the copper chains. Another complication is due to the presence of a staggered field acting on copper spins as they are located at sites that lacks the inversion symmetry. All these reasons make a complete description of the spin dynamics in $(Dy_{0.375}Y_{0.625})_2Cu_2O_5$ solid solution a formidable problem.

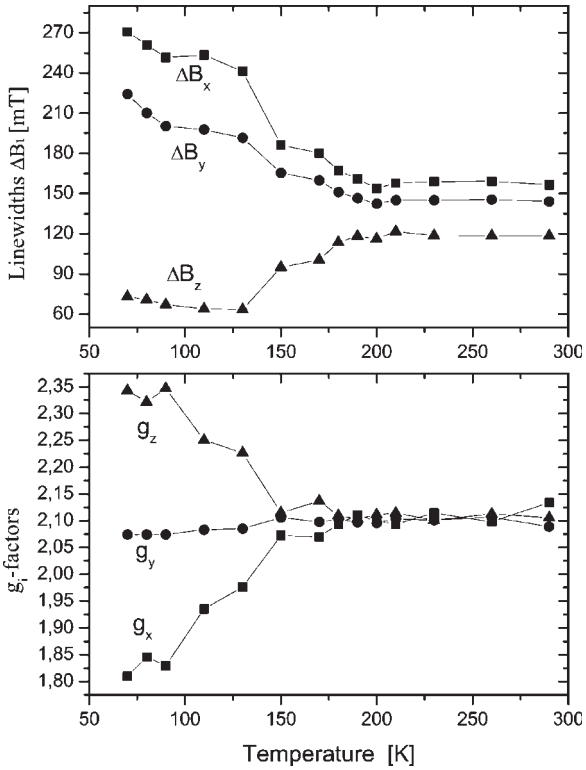

Fig. 6. Temperature dependence of the three anisotropic linewidths ΔB_i (upper panel) and g_i-factors (lower panel) of the decomposed ESR spectra.

4. CONCLUSIONS

Spin dynamics in $(Dy_{0.375}Y_{0.625})_2Cu_2O_5$ solid solution has been studied by using ESR spectroscopy in a wide temperature range. The obtained ESR spectral characteristics have been interpreted in terms of low dimensional magnetism of the copper subsystem. Close to the T_N, temperature dependence of ESR linewidth and resonance field followed clearly the behaviour expected for S=1/2 1D antiferromagnetic quantum chains, while the integrated intensity displayed features characteristic for 2D magnetism. The local internal field, produced by local order of copper spins, develops at temperatures much higher than T_N. Complicated behaviour of the spin systems in $(Dy_{0.375}Y_{0.625})_2Cu_2O_5$ solid solution is the result of strong interaction between the copper and dysprosium magnetic subsystems and the presence of staggered fields acting on the copper spins.

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