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LETTER TO THE EDITOR

Resonance and non-resonance microwave absorption in cobaltites

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Abstract
Microwave studies in the temperature range 4–300 K have been made on the different kinds of cobaltites in an attempt to observe a magnetic resonance. In a $La_{0.9}Ca_{0.1}CoO_3$ single crystal a broad resonance absorption line (with $g \approx 2$) due to the presence of Co^{4+} ions was observed below 40 K. The measured broadening of the linewidth with decreasing temperature can be related to the process of clustering of cobalt ions. In $La_{0.8}Ca_{0.2}CoO_3$ and $TbBaCo_2O_{5.5}$ single crystals non-resonance absorption was observed in the temperature ranges 20–90 and 240–260 K, respectively. In order to investigate the nature of this absorption its intensity was measured as a function of external magnetic field and temperature. The results could suggest that the absorption, although similar for both compounds, was caused by two different mechanisms: microwave power losses on metallic/ferromagnetic clusters in $La_{0.8}Ca_{0.2}CoO_3$ and high-frequency fluctuations of the magnetic domain walls in $TbBaCo_2O_{5.5}$.

1. Introduction

Attention to various cobalt-oxide compounds is part of the general interest in transition-metal oxides exhibiting unusual structural, magnetic and transport properties. Quite recently two classes of cobaltites have attracted considerable interest: cobalt perovskite of the formula $La_{1-x}A_xCoO_3$ (where A = Sr, Ca) and oxygen-deficient layered rare earth cobaltites of the general formula $LnBaCo_2O_{5+\delta}$ (Ln—rare earth, $0 < \delta < 1$). Spin-state transition phenomena [1], charge ordering [2, 3], metal–insulator transitions [4] and a high value of magnetoresistivity [5–12] studied previously in manganites are also observed in cobaltites.

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$La_{1-x}A_xCoO_3$ crystals have Co ions in mixed valence: 3+ and 4+. Depending on the spin state of the ions considered, the Co^{3+}–Co^{4+} pairs can interact ferromagnetically due to the double-exchange interaction, while the Co^{3+}–Co^{3+} and Co^{4+}–Co^{4+} pairs can be coupled antiferromagnetically due to the superexchange interaction. The coexistence and competition of antiferromagnetic and ferromagnetic interactions leads to the frustration, which is responsible for spin-glass ordering observed in cobaltites [13–18]. In the case of low doping it is assumed that the system is separated into hole-rich metallic ferromagnetic clusters with Co^{3+}–Co^{4+} coupling and the hole-poor matrix (phase separation). With increasing doping, the interaction between the hole-rich regions begins and the cluster glass can appear.

Among the various members of the $LnBaCo_2O_{5+\delta}$ family the most interesting seem to be those compounds with $\delta = 0.5$ because of the single valence state (3+) of cobalt ions. In these compounds the paramagnetic to weak ferromagnetic transition occurs at $T_C \sim 280$ K [19–21]. The ferromagnetic phase transforms into the antiferromagnetic one at $T_N \approx 210$–260 K [4, 19, 20, 22].

Co^{3+} and Co^{4+} ions each can exist in three different spin states [4, 5, 23, 24]. Surprisingly, no EPR studies were found in single crystalline cobaltites, in spite of the fact that microwave resonance techniques could provide direct identification of the spin state of the Co ions. On the other hand, non-resonance microwave spectroscopy appears to be useful in investigations of the inhomogeneity of the magnetic structure in doped manganites [25–27]. For cobaltites, the microwave studies were performed for the $La_{0.5}Sr_{0.5}CoO_3$ ceramics and thin films [28, 29]. Also a giant radio-frequency magnetoabsorption effect was found in the cobaltite ceramic $La_{0.5}Sr_{0.5}CoO_3$ [30]. The aim of the present work is to shed some more light on the characterization of the $La_{1-x}Ca_xCoO_3$ ($x = 0.1, 0.2$) and $TbBaCo_2O_{5.5}$ single crystals using EPR and non-resonance microwave spectroscopy.

2. Experimental details and results

The sample's structure and preparation has been described previously [22, 31]. The microwave magnetic measurements were made using the X-band reflection cavity EPR spectrometer operating at the fixed frequency of about 9.25 GHz with a variable temperature cryostat (Oxford Instruments Model 1104). The field derivative of microwave power absorption was registered as a function of DC magnetic field **B** that could be changed from 0 to 1 T. Computer integration of the experimental curves, showing non-resonance absorption, was performed to obtain the amplitude of the microwave power absorption. The additional magnetization measurements were performed using a SQUID magnetometer (Quantum Design MPMS-5).

No EPR signal has been detected in $La_{0.9}Ca_{0.1}CoO_3$ down to 45 K. A broad resonance line appears at about 43 K. The inset in figure 1 shows an example of this spectrum recorded at $T = 22$ K. The line is centred at about 3 kOe ($g \approx 2$) with an asymmetrical profile. Its position almost does not depend on **B** orientation with respect to the sample's crystallographic axes. The single EPR line observed in the crystal indicates an effective spin $S_{eff} = 1/2$ of the paramagnetic centre. It suggests that the resonance would be related to Co^{4+} ions in the low spin state (t_{2g}^5, $S = 1/2$). Co^{3+} ions could be in the low spin state (t_{2g}^6, $S = 0$) or the intermediate spin ($t_{2g}^5 e_g^1$, $S = 1$) state. In the first case (non-magnetic state of Co^{3+} ions), both the integrated intensity of the EPR line $I(T)$ as well as the magnetic susceptibility $\chi(T)$ of the sample should be described by the same temperature dependence. However, the comparison of these dependences (figure 1) showed their different behaviours. It means that a part (or even all) of the Co^{3+} ions are not in the low spin state. Probably, they are in the intermediate spin state and are strongly coupled to the lattice, being practically invisible in the common EPR experiment.
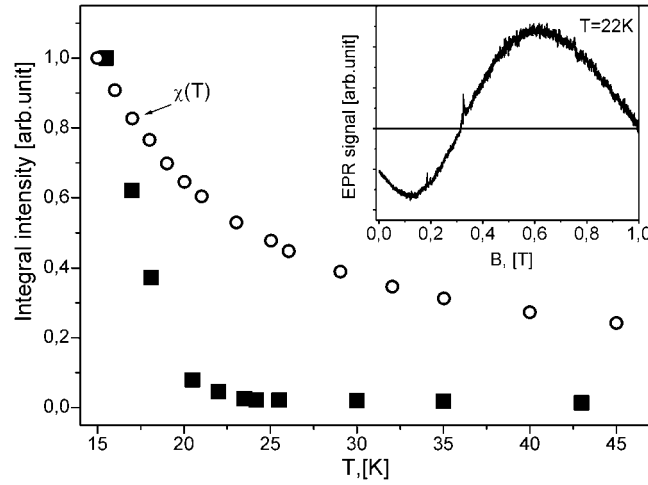
Figure 1. Temperature dependence of the integral intensity $I(T)$ (■) of the EPR spectrum and magnetic susceptibility $\chi(T)$ (O) in a $La_{0.9}Ca_{0.1}CoO_3$ single crystal. Both $I(T)$ and $\chi(T)$ are shown in arbitrary units and normalized to 1 for comparison. The inset show an example of the EPR spectrum recorded at 22 K.
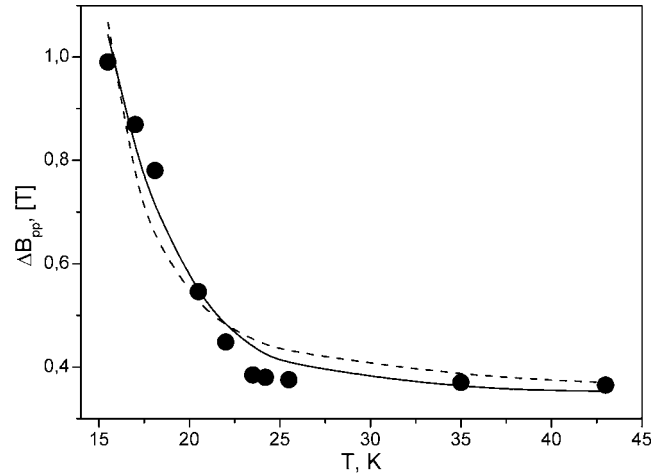

Figure 2. Temperature dependence of the linewidth (●) of the EPR spectrum in a $La_{0.9}Ca_{0.1}CoO_3$ single crystal. The broken and full curves represent the least squares fit of equations (1) and (2), respectively.

Figure 2 shows the temperature dependence of linewidth, ΔB_{pp} (determined as a peak-to-peak value of the first derivative of the absorption curve). As one can see, ΔB_{pp} increases sharply with lowering the temperature. Below 15 K the line broadens strongly and it is difficult to estimate credibly its linewidth. The EPR linewidth variation with temperature was analysed using two different expressions. The first, assuming that the change in linewidth is attributed to the spin-glass to paramagnet transition at T_f, based on the known expression for critical effects (see, for example, [32]) and taking into account all the limitations in the discussed case (see [33] and the discussion in this paper):

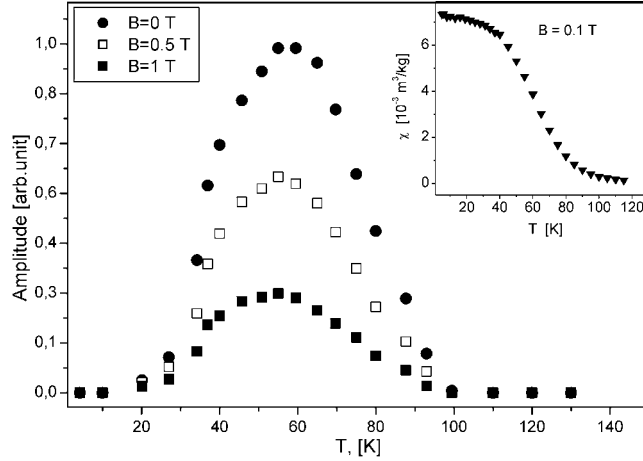$$\Delta B_{pp} = \Delta B_0 + A \left(\frac{T_f}{T - T_f} \right)^{\alpha}, \tag{1}$$

Figure 3. Temperature dependence of microwave absorption amplitude in a $La_{0.8}Ca_{0.2}CoO_3$ single crystal at different values of the magnetic field. The inset shows the DC magnetic susceptibility $\chi(T)$ in 0.1 T in a $La_{0.8}Ca_{0.2}CoO_3$ single crystal.

where ΔB_0 is the temperature-independent part of the linewidth, A is a constant, α is the critical exponent and T_f is the phase transition temperature. The broken curve in figure 2 represents the best fit of equation (1) to the experimental data with the following set of parameters: $\Delta B_0 = 350 \pm 13$ mT, $A = 105 \pm 10$ mT, $\alpha = 1.7 \pm 0.5$ and $T_f = 11.7 \pm 0.8$ K.

The second approach is based on the assumption that the broadening of ΔB_{pp} is due to the spatial inhomogeneity which must be present with the random distribution of Ca ions, and which results in an effective clustering of Co atoms. Variation of ΔB_{pp} due to this effect can be described using the following expression [34]:

$$\Delta B_{pp} = \Delta B_0 + \Gamma e^{-T/T_0}, \tag{2}$$

where Γ is a constant and a parameter T_0 corresponds to the potential barrier separating two neighbouring ground states of the disordered spin system. The full curve in figure 2 represents the best fit of equation (2) to the experimental data with the following values of the parameters: $\Delta B_0 = 353 \pm 7$ mT, $\Gamma = 38 \pm 11$ T and $T_0 = 3.8 \pm 0.3$ K.

Comparing the fitted results, it should be remarked that the second model better describes the linewidth variation on temperature (using a simpler expression with three parameters, whereas the first model needs four parameters). Moreover, magnetic DC susceptibility (measured in the zero-field cooling regime in $B = 10$ mT) has a maximum at $T = 5$ K, interpreted usually as the freezing temperature. Upon increasing the measuring field this maximum shifts down and, at $B = 100$ mT, is below 2 K. One could suspect that the position of this peculiarity correlates to some extent with the value of $T_0 = 3$ K.

For $La_{1-x}Ca_xCoO_3$ with higher doping, i.e. $La_{0.8}Ca_{0.2}CoO_3$, instead of a resonance with the usual character, a microwave absorption peak with quite unusual characteristics was observed. To show the effect quantitatively, in figure 3 temperature dependences of the absorption amplitude are shown at various values of the applied external magnetic field. It is seen that absorption appears in the temperature range 20–100 K. The maximum of absorption at all temperatures is observed in the absence of a magnetic field. The amplitude of absorption only slightly depends on the orientation of the magnetic field. It should be mentioned that the upper limit of this effect corresponds well (see inset in figure 3) to the beginning of
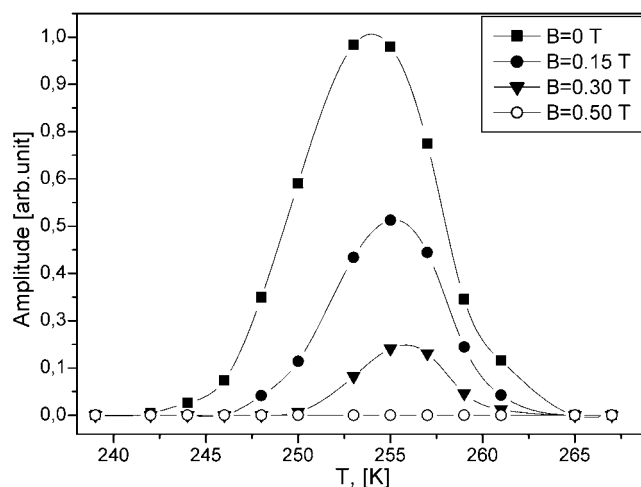
Figure 4. Temperature dependence of microwave absorption amplitude in a TbBaCo$_2$O$_{5.5}$ single crystal at three different values of magnetic field **B**. **B** was applied perpendicular to the c axis (parallel to [110] direction), while the microwave field was parallel to the c axis. Curves connecting points are only guides for the eyes.

the substantial growth of DC magnetic susceptibility (magnetic properties of La$_{1-x}$Ca$_x$CoO$_3$ single crystals will be published elsewhere).

Qualitatively similar non-resonance microwave absorption was observed in TbBaCo$_2$O$_{5.5}$ single crystals in the temperature range 240–265 K. The amplitude of this absorption versus temperature is shown in figure 4. Similarly, as in the case of La$_{0.8}$Ca$_{0.2}$CoO$_3$, the microwave absorption is maximal when the magnetic field is zero. Enlarging the applied magnetic field suppresses the absorption and shifts slightly its maximum from 254 K at **B** = 0 to 256 K for a field of about 3 kOe. In the case of TbBaCo$_2$O$_{5.5}$, there are also two important peculiarities that differentiate the absorption from that in La$_{0.8}$Ca$_{0.2}$CoO$_3$. First of all, in this case it is strongly anisotropic: the absorption appears only when **B** is perpendicular to the c axis (or **B** || ab plane), which means that (in the EPR spectrometer applied) the microwave field is parallel to the c axis. If **B** is rotated in the ab plane of the crystal, the absorption changes relatively weakly, although it is the highest as **B** coincides with the $\langle 110 \rangle$ directions, and such a configuration was used to obtain the results presented in figure 4. The second peculiarity is the fact that a strong enough magnetic field completely suppresses this absorption. As was shown in figure 4, the application of a field as strong as 0.5 T was enough that the absorption disappeared.

3. Discussion and conclusion

The thermal variations of the EPR linewidth in La$_{1-x}$Ca$_x$CoO$_3$ single crystals ($x = 0.1$), as well as the asymmetrical profile of the resonance line, are typical of the spin-glass-like systems. The observed resonance line is an envelope of all individual lines contributed by separated magnetic complexes/clusters containing Co^{4+} ions. The sharp increase of the linewidth is due to a growth of local magnetic inhomogeneities, attributed to the competition between long-range dipolar interactions and short-range exchange interactions. With the lowering of temperature the number of clusters grows, intensifying the resonance absorption.

By an increase in the x value (i.e. doping of Ca), the creation and development of ferromagnetic/metallic states could be expected as a result of the inhomogeneous distribution of the Ca^{2+} ions. The material divides into the hole-rich FM metallic clusters (near the

Ca ions) and the hole-poor semiconducting matrix (similar to the Sr-doped cobaltites [35]). The magnetization studies of $La_{0.8}Ca_{0.2}CoO_3$ had shown the existence of phase separation and the changes in magnetization were interpreted as an evolution of the spin clusters [31]. Therefore it is obvious to assume that microwave losses on metallic clusters are at least one of the reasons for the appearance of non-resonance absorption. These losses will be strictly related to the conductivity (similar to the papers of Belevtsev [28, 29]). As it follows from magnetization studies [31], with a decrease in temperature the volume and numbers of spin clusters would increase. Thus the total absorption surface is increasing where microwave power can be dissipated/absorbed. It shows a growth in absorption when the temperature decreases from 100 K down to $\sim$55 K (see figure 3). Upon further reductions in temperature, interaction between clusters begins and then a percolation threshold could be reached. In that case, a microwave field cannot penetrate all of the crystal because of its shielding by a spreading/growing metallic surface. As microwave power interacts with a smaller part of crystal its losses decrease, leading to a decrease in the absorption when the temperature is lower than 55 K. The dependence of the absorption amplitude on the magnetic field strength could arise from the magnetoimpedance (MI) effect. This effect was studied extensively in Co-based amorphous alloys [36, 37]. In terms of the MI effect description, the complex surface impedance $Z \approx \sqrt{\omega\mu/\sigma}$, where ω is the frequency and μ and σ are the complex permeability and conductivity, respectively. An application of a magnetic field leads to the growth of initial permeability and a reduction in σ by reducing the mobility of the electrons. Therefore, changes of both μ and σ should be considered as a source of a magnetic field dependence of the microwave absorption. The impedance increases in magnetic field that, in turn, suppresses absorption.

The strong anisotropy of microwave absorption observed in $TbBaCo_2O_{5.5}$ single crystals leads to the conclusion that the mechanism responsible for the appearance of absorption in $TbBaCo_2O_{5.5}$ is other than that in $La_{0.8}Ca_{0.2}CoO_3$. As follows from magnetization studies of $TbBaCo_2O_{5.5}$ [22], this system is in the weak ferromagnetic phase in the temperature range 210–277 K. In this temperature range, the system displays hysteresis loops, which were explained by existence of magnetic and crystallographic domain structures. It is important to highlight that hysteresis loops exists only in a limited range of magnetic fields (below $\sim$0.5 T). Thus it is supposed that the magnetic domain structure should vanish at higher fields and this coincides with the fact that microwave absorption has also disappeared at $\mathbf{B} > 5$ kOe (shown in figure 4). $TbBaCo_2O_{5.5}$ exhibits a metal–insulator transition at $T_{MI} \sim 340$ K and is insulating below T_{MI} [4]. Therefore conductivity cannot be the main source of microwave absorption. The microwave absorption near T_C seems to be inherent for weak ferromagnetic systems since it was observed also in rare earth orthoferrites [38, 39]. As was shown in [39], that absorption may be attributed to the high-frequency fluctuations of domain walls. These facts together with experimental results, presented in this paper, allow us connect the absorption in $TbBaCo_2O_{5.5}$ with the presence of magnetic domain structures.

There is no theoretical approach, to the best of our knowledge, describing the dynamics of a magnetic domain in a microwave magnetic field for weak ferromagnets (probably due to the complexity of the problem), but such a theory was developed for ferromagnets [40]. In addition to a well known low-frequency branch of domain wall translations, the theory [40] predicts the existence of high-frequency branches in the spectrum of the wall excitations that involves both: the wall translations and oscillations transverse to the wall plane. By measuring the absorption as a function of frequency, it would be possible to find the value of the resonance frequency where the absorption will have a maximum. In this work the spectrometer with a fixed microwave frequency was used, which is why the data, reported in this paper, are related to the non-resonance absorption.

The amplitude of microwave absorption depends first of all on the total volume of domain walls and reaches a maximum (figure 4) at 254–256 K. This coincides very well with the position of the susceptibility maximum (at 258 K for corresponding field values) [22]. The amplitude decreases with increase of **B** because the total amount of domain walls decreases.

4. Summary

Microwave studies have been performed on $La_{1-x}Ca_xCoO_3$ ($x = 0.1, 0.2$) and $TbBaCo_2O_{5.5}$ single crystals. In $La_{0.9}Ca_{0.1}CoO_3$ the resonance absorption is observed, being related to the presence of Co^{4+} ions. In $La_{1-x}Ca_xCoO_3$ the increase in doping of Ca ions leads to the formation of ferromagnetic metallic clusters, which are sources of non-resonance microwave absorption. It has been suggested that non-resonance microwave absorption is due to microwave power losses in the surface layer of metallic ferromagnetic clusters. In $La_{0.8}Ca_{0.2}CoO_3$ the non-resonance absorption appears in the low-temperature region ($T < 100$ K), where the average size of the ferromagnetic cluster is distinctly enlarged.

In $TbBaCo_2O_{5.5}$ another mechanism for non-resonance absorption, observed at 240–265 K, has been proposed related to the weak ferromagnetic state existing at these temperatures. The appearance of this kind of absorption can be explained by high-frequency fluctuations of the magnetic domain walls.

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