

Splitting of low-temperature magnetic transition in $\text{Dy}_2\text{BaCuO}_5$

M. N. Popova and G. G. Chepurko

Institute of Spectroscopy, Academy of Sciences of the USSR

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The optical spectra of the “green phase” of $\text{Dy}_2\text{BaCuO}_5$ and of the dilute compound $\text{Dy}_{0.02}\text{Y}_{1.98}\text{BaCuO}_5$ have been studied. The low-temperature magnetic transition in $\text{Dy}_2\text{BaCuO}_5$ was found to split into two first-order phase transitions: at $T_{N2} = 11.26$ K the rare-earth subsystem becomes ordered; the transition that follows at $T_R = 11.08$ K evidently corresponds to a spin reversal. The copper subsystem becomes ordered at $T_{N1} = 20 \pm 0.5$ K in $\text{Dy}_2\text{BaCuO}_5$ and for $T_N = 14.5$ K in $\text{Dy}_{0.02}\text{Y}_{1.98}\text{BaCuO}_5$.

Considerable experimental evidence shows that antiferromagnetism and superconductivity are closely related in new high- T_c superconductors. High- T_c superconductivity mechanisms in which magnetic interaction plays a dominant role have been suggested (see, for example, Ref. 1). The magnetic properties of not only high- T_c superconductors, but also of compounds related to them are accordingly being studied in detail. The so-called “green phases” R_2BaCuO_5 with $R = \text{Sm-Lu}$ and Y are formed in the phase triangle $\text{R}_2\text{O}_3\text{--BaO--CuO}$ which contains a high- T_c superconductor $\text{R}_2\text{BaCu}_5\text{O}_{7-x}$. The structure of these green phases is described in detail in Refs. 2 and 3. We will mention here only the following point which is relevant in our discussion below: there are two nonequivalent fourfold sites for the R^{3+} ion, both of which have a local symmetry C_{4v} .¹⁾

It was found that the Y_2BaCuO_5 compound has magnetic order, and that the magnetic moments of copper form a noncolinear antiferromagnetic structure. But values ranging from 14 K to 35 K were obtained for the Néel temperature T_N .⁴⁻⁸ Two magnetic transitions in the rare-earth compounds R_2BaCuO_5 were recently observed.^{9,10} The high- T_c transition was interpreted as an antiferromagnetic transition-ordering of the copper subsystem ($T_{N1} = 17\text{--}20$ K), while the low-temperature transition was attributed to the antiferromagnetic ordering of the rare-earth subsystem ($T_{N2} = 5\text{--}10$ K).^{9,10} Using an optical spectroscopy method, we showed that the low-temperature transition in $\text{Dy}_2\text{BaCuO}_5$ occurs in two stages.

We studied $\text{Dy}_2\text{BaCuO}_5$ and $\text{Dy}_{0.02}\text{Y}_{1.98}\text{BaCuO}_5$ polycrystalline samples. The optical spectra of the diffuse reflection at temperatures 2.2–40 K in the spectral regions near 6000 cm^{-1} (the ${}^6H_{15/2} \rightarrow {}^6H_{11/2}$ transition in a Dy^{3+} ion), 7900 cm^{-1} (${}^6H_{15/2} \rightarrow {}^6H_{9/2} + {}^6H_{11/2}$), and 9000 cm^{-1} (${}^6H_{15/2} \rightarrow {}^6H_{7/2} + {}^5F_{9/2}$) were obtained by using a high-resolution Fourier spectrometer, where an InSb photodiode was used as a detector (the procedure used to obtain these spectra is described in Ref. 11, for example).

The absorption of $\text{Dy}_2\text{BaCuO}_5$ near a spectral transition in a Dy^{3+} ion is shown in Fig. 1. A comparison of the spectra of a concentrated system and a dilute system at

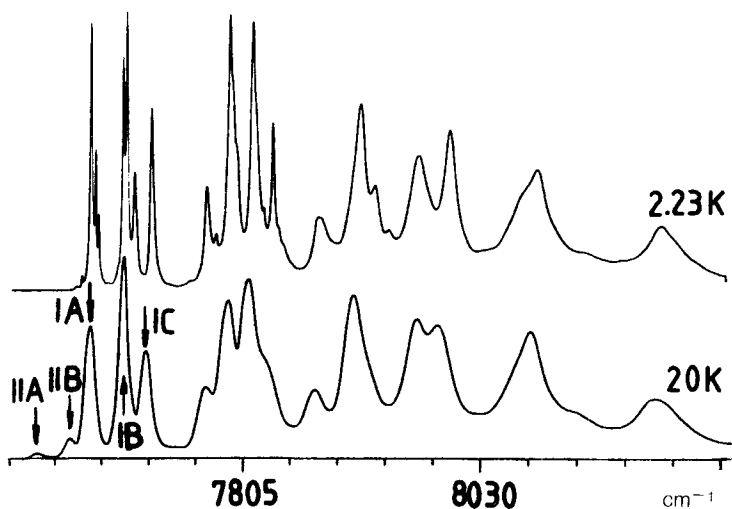


FIG. 1. Absorption of $\text{Dy}_2\text{BaCuO}_5$ near the ${}^6H_{15/2} \rightarrow {}^6H_{9/2} + {}^6F_{11/2}$ transition in the Dy^{3+} ion. The low-frequency lines are identified in accordance with the diagram in Fig. 2, without dividing them in half.

20 K (when all the magnetic moments are disordered) shows that the number of lines and the manner in which they are grouped are the same in both cases. The number of lines is greater than the maximum permissible number without a magnetic field, which is attributable to the presence of two nonequivalent sites in the structure. The frequencies of the lines are different in the concentrated and dilute systems, possibly because of the difference in the interionic distances, and hence the difference in their crystal fields. The large width of the spectral lines in the concentrated system ($9\text{--}12\text{ cm}^{-1}$ for low-frequency lines²⁾ in comparison with $3\text{--}4.5\text{ cm}^{-1}$ in a dilute system) stems from a rare-earth interaction. We found from the spectral data the value $51 \pm 2\text{ cm}^{-1}$ for the energy of the first excited level of the Dy^{3+} ion in $\text{Dy}_2\text{BaCuO}_5$.

The spectral method of analyzing the magnetic phase transitions is based on recording the splitting of the Kramers doublets in the case of magnetic ordering. The spectral line in this case generally splits into four components, as shown schematically in Fig. 2. Figure 2a shows a temperature transition of the spectral lines in $\text{Dy}_{0.02}\text{Y}_{1.98}\text{BaCuO}_5$, which can naturally be compared with the magnetic ordering of copper in this compound (see also Ref. 4). At $T_N = 14.5\text{ K}$ the single lines split, the splitting increases as the temperature is further lowered, the intensities of the long-wavelength components decrease (in accordance with the decrease in the population of the upper component of the split, ground-state Kramers doublet), and the lines contract. The corresponding spectral lines of $\text{Dy}_2\text{BaCuO}_5$ behave in a similar manner in the high-temperature region between $T_{N1} \simeq 20\text{ K}$ and $T \simeq 11.3\text{ K}$. At a temperature of 11.26 K the splitting varies spasmodically and the lines narrow rapidly. At 11.18 K on more abrupt change in the splitting occurs. Figure 3 shows typical parts of the splitting and the width of a line as a function of temperature. Also shown in this figure is the splitting of the corresponding line in the spectrum of a dilute system.

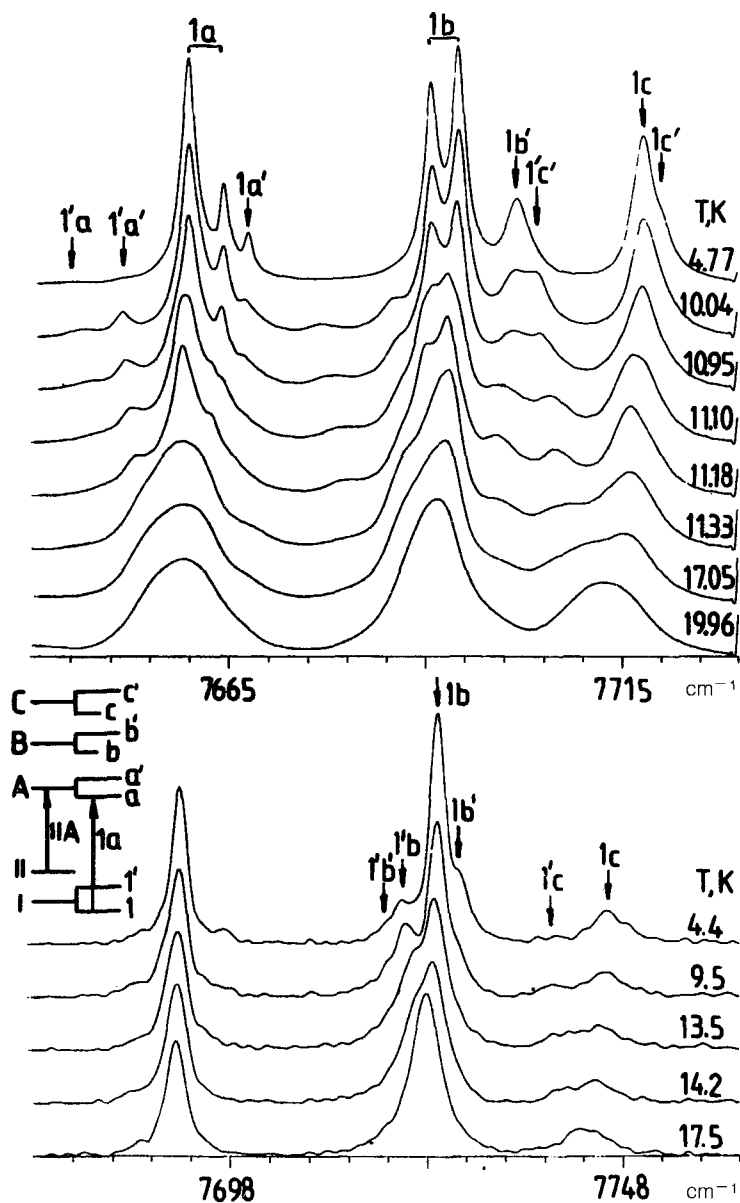


FIG. 2. Temperature transformation of the spectrum. (a) $\text{Dy}_{0.02}\text{Y}_{1.98}\text{BaCuO}_5$ and (b) $\text{Dy}_2\text{BaCuO}_5$ near the low-frequency lines of the ${}^6H_{15/2} \rightarrow {}^6H_{9/2} + {}^6F_{11/2}$ transition in the Dy^{3+} ion. The identification of lines according to the diagram shown on the side was made on the basis of the position and temperature dependence of the line intensities.

We attribute the high-temperature transition in $\text{Dy}_2\text{BaCuO}_5$, as do the authors of Ref. 10, to the antiferromagnetic ordering of the copper subsystem. Evidence in support of this interpretation also comes from a comparison with the results for a low-concentration compound $\text{Dy}_{0.02}\text{Y}_{1.98}\text{BaCuO}_5$, where the Dy^{3+} ion is actually affect-

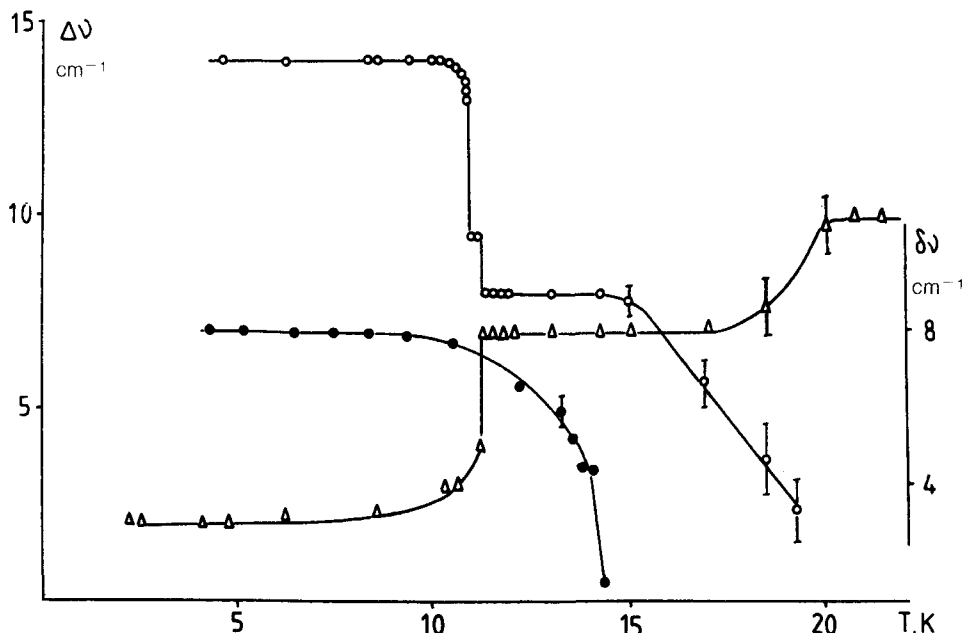


FIG. 3. Temperature dependence of the splitting $\Delta\nu$ (open circles) and the half-width $\delta\nu$ (triangles) of the absorption line near 7714 cm^{-1} in $\text{Dy}_2\text{BaCuO}_5$ and the splitting of the line corresponding to it in $\text{Dy}_{0.02}\text{Y}_{1.98}\text{BaCuO}_5$ (filled circles).

ed only by the copper subsystem: At $T_N = 14.5\text{ K}$ empty ferromagnetic ordering of copper in this compound causes approximately the same splitting of spectral lines as the high-temperature transition in $\text{Dy}_2\text{BaCuO}_5$ (Fig. 3). On the basis of our data, the temperature at which the copper subsystem becomes ordered is $T_{N1} \approx 20\text{ K}$ and on the basis of the measurements of the heat capacity it is 18 K .¹⁰

The abrupt change in the splitting at $T_{N2} = 11.26\text{ K}$, which is accompanied by a rapid narrowing of the spectral lines (until they reach the width they have in the dilute system), can naturally be compared with the magnetic ordering of the rare-earth subsystem, which stops the dipole broadening of the levels because of the interaction with the large, direction-changing magnetic moments of Dy^{3+} in a concentrated disordered system. The next abrupt change in the splitting, which occurs at approximately the same temperature, may be due to the spin-flip transition, $T_R = 11.08\text{ K}$. Clearly, the spin configuration formed at T_{N2} is unstable and a further lowering of the temperature by $\Delta T \geq 0.18\text{ K}$ causes it to change. The domains of the two phases coexist in a very narrow temperature interval ($\Delta T \approx 0.15\text{ K}$) (see the spectrum at $T = 11.10\text{ K}$ which is a superposition of the spectra before and after the transition): we are dealing here with a type-I phase transition. We have thus been able to observe (by using a spectral method) the splitting of a low-temperature magnetic transition in $\text{Dy}_2\text{BaCuO}_5$ into two successive transitions (apparently the ordering of a rare-earth subsystem and a spin-flip transition). Our transition near 10 K was recorded from the measurements of the heat capacity and susceptibility.¹⁰

Analysis of all the spectral data leads to the following values of the exchange splitting of the ground state of dysprosium in $\text{Dy}_2\text{BaCuO}_5$: $\Delta = 7 \pm 1.5 \text{ cm}^{-1}$ for $T_{N2} < T < T_{N1}$ and $\Delta = 14 \pm 2 \text{ cm}^{-1}$ for $T < T_R$ (in both positions). For Dy^{3+} in Y_2BaCuO_5 we have $\Delta = 7 \pm 1 \text{ cm}^{-1}$. For comparison, note that in $\text{Dy}_2\text{Cu}_2\text{O}_5$ $\Delta = 13 \text{ cm}^{-1}$ according to our spectral data, and the copper subsystem and rare-earth subsystem in this compound become ordered at the same temperature: $T_N = 11 \text{ K}$ (Ref. 12 and our measurements). The narrowest lines in $\text{Dy}_2\text{BaCuO}_5$ have an additional splitting ($3\text{--}4 \text{ cm}^{-1}$) of the components of the transition between the split Kramers sublevels, which is absent in the dilute system (lines 1a and 1b in Fig. 2b). This is clearly a Davydov splitting which occurs as a result of the interaction of the equivalent dysprosium ions with each other in the unit cell. Of the four such ions, we can isolate two identical pairs with a considerably weaker interaction between the pairs than that within them. This explanation accounts for the fact that the Davydov splitting is into two components, rather than four.

We note, in conclusion, that the R_2BaCuO_5 compounds, in terms of their magnetic properties, are intermediate compounds between $\text{R}_2\text{Cu}_2\text{O}_5$ and the tetragonal phase of the high- T_c superconductor $\text{RBa}_2\text{CuO}_{7-x}$: As in high- T_c superconductors, the copper and the rare-earth magnetic subsystems are weakly bound in them, which accounts for the distinct ordering in terms of temperature (although the difference in T_{N1} and T_{N2} is not as great as it is in a high- T_c superconductor). At the same time, the magnetic moments of copper in them, as in $\text{R}_2\text{Cu}_2\text{O}_5$, are localized.^{10,12}

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¹⁾ A crystal field of such a low symmetry splits the levels of the rare-earth ion with an odd number of electrons (as that in Dy^{3+}) into Kramers doublets.

²⁾ The rf lines are additionally broadened because of phonon relaxation.

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