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High-resolution spectroscopy of rare earth cuprates and nickelates

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Abstract

This presentation gives a brief review of the work on the $R_2Cu_2O_5$ (R=Tb-Lu, Y, Sc, In) and R_2BaMO_5 (R=Nd, Sm-Gd, Dy-Lu and Y, M=Cu, Ni) cuprates and nickelates, performed by the author's group. We measured high-resolution optical absorption spectra of an intrinsic R^{3+} ion or Er^{3+} probe in these compounds, by means of a Fourier transform spectrometer. On the basis of these spectra, we investigated crystal field splittings of the rare-earth energy levels, magnetic ordering, low-dimensional magnetic correlations, the arrangement of magnetic moments of transition metal ions and peculiarities of spin-reorientation phase transitions. We have registered for the first time, magnetic phase transitions, some of them not detectable by other methods, in R_2BaCuO_5 with R=Nd, Dy, Yb, Lu, Y and in R_2BaNiO_5 with R=Nd, Sm, Gd, Eu, Dy, Ho, Tm, Lu. © 1998 Elsevier Science S.A.

Keywords: Fourier transform spectroscopy; $R_2Cu_2O_5$; R_2BaMO_5 (M=Cu, Ni)

1. Introduction

This presentation is devoted to the high-resolution optical spectroscopy of rare-earth (RE) cuprates and nickelates from the families $R_2Cu_2O_5$ (R=Tb-Lu, Y, Sc, In) and R_2BaMO_5 (R=Nd, Sm-Gd, Dy-Lu and Y, M=Cu, Ni). These compounds first attracted attention in connection with the high-T_c superconductivity problem, because most of them were found as accompanying phases in the synthesis of 1-2-3 high-T_c superconductors. It turned out later that they have interesting magnetic properties and deserve to be studied in connection with the problem of low-dimensional magnetism. There are CuO planes in the structure of 'blue phases' $R_2Cu_2O_5$, with intraplane Cu–Cu distances considerably smaller than the interplane ones. The so called 'green phases' R_2BaCuO_5 (R=Y, Sm-Lu) and 'brown phase' Nd_2BaCuO_5 of R-Ba-Cu-O superconducting ceramics contain isolated Cu^{2+} ions not interconnected by direct bonds through one oxygen. Various Cu–O–O–Cu or Cu–O–R–O–Cu superexchange paths, low-dimensional in particular, may dominate in these compounds, depending on the particular R^{3+} ion. R_2BaNiO_5, with R=Lu and Yb, are isostructural to the green phases while the other members of this family, with R=Y, Nd-Gd, Dy-Tm, have completely different structures containing isolated -Ni–O–Ni- chains.

All the above mentioned compounds contain both rare-earth ions (f-ions) and magnetic Cu^{2+} and Ni^{2+} ions (d-ions). While the optical transitions within the d-shell result in broad (with a half-width of several hundreds and even thousands wave numbers) smooth bands, the transitions within the f-shell, which is well screened by the outer p- and s-shells, lead to extremely narrow spectral lines. They allow to probe the local environment of an f-ion (see, e.g., [1]), to study a crystal field [2], to investigate electron–phonon [2], hyperfine [3] and ion–ion [4] interactions and to detect very fine isotope effects [5]. In magnetic materials, there is just the exchange and magnetic dipole interactions between the various ions, which drive a crystal into a magnetically ordered state. As a result, a local magnetic field appears at the rare-earth site and splits or shifts the energy levels of the RE ion. Earlier works have shown that the method of RE spectroscopic probe complements substantially, other methods of investigating magnetic f–d compounds (Ref. [6] which deals with magnetic and optical studies of $ErCrO_3$ can be indicated as an example).

Typically, the spectral resolution of grating spectrometers used for such studies is 0.5–1 cm^{-1} in the visible range [6]. As we have shown [5], inhomogeneous widths of some RE spectral lines can be as small as 0.007 cm^{-1}. The most intense, allowed in free-ion optical transitions, lie in the infrared and occupy broad spectral regions for the majority of RE^{3+} ions. It is advantageous to register such spectra by a Fourier transform spectrometer rather than by a classical one [7]. Substantial gain in sensitivity enables one to study weak spectra, not available before, of RE ions introduced in a small amount as a probe into a magnetic material. High spectral resolution and absolute wave number precision in Fourier transform spectroscopy make

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it possible to measure small line splittings and shifts and also to register the shape of spectral lines.

My group investigated $R_2Cu_2O_5$ and R_2BaMO_5 (M=Cu, Ni) compounds for several years by means of high-resolution Fourier transform spectroscopy. A brief review of this work is given below.

2. Experimental

Polycrystalline samples of $R_2Cu_2O_5$ (R=Tb-Lu, Y, Sc, In) and R_2BaMO_5 (R=Nd, Sm-Gd, Dy-Lu and Y, M=Cu, Ni) compounds, pure or with erbium introduced as a spectral probe (typically, 1 at.%), were prepared from oxides by solid-state reaction in air. The samples were tested by X-ray diffraction and were found to be single phase.

To take the spectra of these polycrystalline samples, opaque in some cases, we have developed a special technique [8]. The powder samples were carefully ground, mixed with ethanol and put on the sapphire platelet directly before the window of an InSb detector. The whole assembly was inside an optical cryostat, either in liquid helium or in cold helium vapor. Near infrared spectra due to optical transitions in the intrinsic R^{3+} ion or Er^{3+} probe were registered at 2–120 K with a spectral resolution up to 0.06 cm^{-1} employing a BOMEM DA3.002 Fourier transform spectrometer. In fact, we measured diffuse transmittance spectra. Absorption spectra were then calculated by an appropriate computer program. The width of some spectral lines in our samples at 2 K was as small as 0.1 cm^{-1}.

3. Rare-earth spectra and hierarchy of interactions in $R_2Cu_2O_5$ cuprates

A crystal field of any symmetry lower than a cubic one lifts all but the Kramers degeneracy of the levels of a free RE ion with an odd number of electrons. Kramers doublets are further split by magnetic interactions in a magnetically ordered state. Each spectral line splits into a maximum of four components (see Fig. 1). To answer the question on what kind of interactions and which ions contribute decisively to these splittings in the *f–d* magnetic compounds, let us consider an example of the best studied [9–11] family: $R_2Cu_2O_5$.

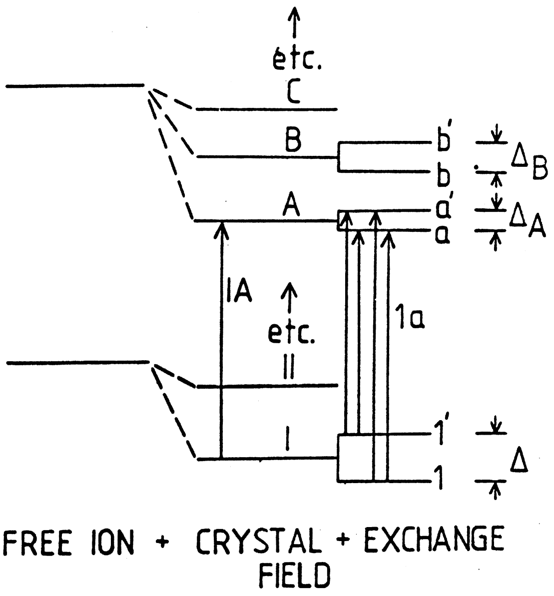

Fig. 1. Levels of a Kramers ion in a magnetically ordered crystal.

Fig. 2 presents the absorption spectrum of $Er_2Cu_2O_5$, both in paramagnetic and magnetically ordered states. Fig. 3 shows in more detail the splitting of one spectral line due to the establishment of a magnetic order. There are two nonequivalent crystallographic positions for the R^{3+} ions in the crystal structure. Spectral lines originating from each of them overlap at high temperatures but are clearly resolved in the low-frequency part of the low-temperature spectrum of Fig. 2. An example of an identification of the spectral lines is given in Fig. 3. The appropriate Kramers level splittings can be determined.

We introduce now the Er^{3+} probe into the whole series of $R_2Cu_2O_5$ cuprates, and it turns out that these splittings are similar in $R_2Cu_2O_5$ with R=Y, Lu, Er and Tb (Table 1 lists the ground-state splittings). These are cuprates with strongly different R ions (Y and Lu have no magnetic moment, the Er and Tb magnetic moments order differently [12,13]) but with an identical structure of copper magnetic moments μ_{Cu}.

Thus, the level splittings of the Er^{3+} ion in these compounds are mainly due to the Er–Cu interactions, the Er–R ones being negligible. Moreover, the short-range exchange interaction must dominate over the magnetic dipole one. This follows from the fact that μ_{Cu} is considerably smaller than μ_{Er} and μ_{Tb} ($\simeq 1.0\mu_B$, which may be compared with $\simeq 5\mu_B$ for Er and Tb [12,13], μ_B being the

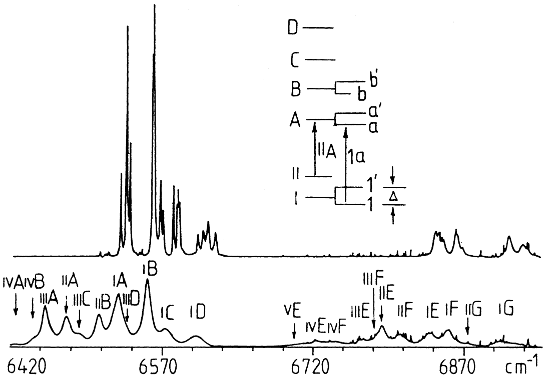

Fig. 2. Absorption in the region of the ${}^4I_{15/2} \rightarrow {}^4I_{13/2}$ transition in $Er_2Cu_2O_5$ at 88 K>T_N (lower trace) and 6.2 K<T_N (upper trace). Very sharp lines in the high frequency part of the spectrum are due to the absorption by residual water vapor.

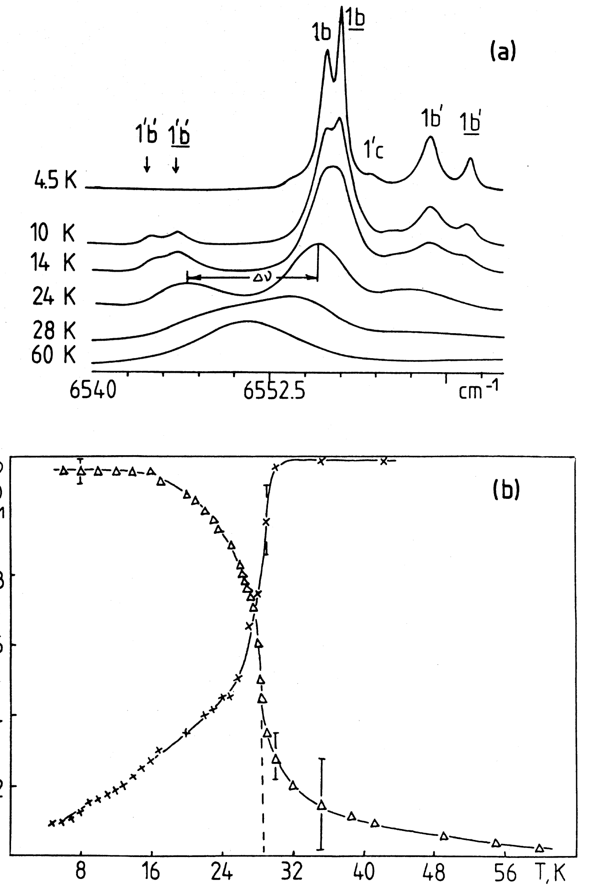

Fig. 3. The absorption line IB in $Er_2Cu_2O_5$ at different temperatures and the temperature dependencies of its splitting $\Delta\nu$ (triangles) and of the half-width of the component 1a (crosses). The underlined notations refer to the second position in the structure.

Bohr magneton) while the distances Er–Cu and Er–R have close values [13,14], and so the Er–R magnetic dipole interaction is greater than the Er–Cu one. In summary, the Er^{3+} probe level (and spectral line) splittings are determined, basically, by the ordering of the nearest copper magnetic moments. Consequently, these splittings reflect a short-range order in the copper magnetic subsystem and, evidently, depend essentially on the correlations between the magnetic moments of the closely situated copper ions.

The inset of Fig. 4 shows the temperature behavior of the correlation functions $\Gamma_r(T)$ ($r=1, 2, \ldots \infty$) for a given ion and its neighbours from the coordination sphere number r [15]. As a short-range order remains at $T>T_c$, the $\Gamma_r(T)$ functions with $r\neq\infty$ are nonzero at $T>T_c$. They have a point of inflection at $T=T_c$. The values of $\Gamma_r(T=T_c)$ enter into the expression for the magnetic energy of a system at $T=T_c$, and they are the greater (and correspondingly, the 'tails' of the Γ_r ($r\neq\infty$) functions at $T>T_c$ are the longer) the lower is the dimensionality of a magnetic system [15]. If we now turn our attention to the experimental dependencies $\Delta\nu(T)$, in Fig. 3(b) and Fig. 4, of the line-splitting on temperature, the close resemblance between $\Delta\nu(T)$ and $\Gamma_r(T)$ is seen. Therefore, it seems natural to determine the temperature of a magnetic ordering T_c as the abscissa of the point of inflection in the curve $\Delta\nu(T)$ and to look for low-dimensional magnetism by examining the 'tails' of spectral line splittings at $T>T_c$.

Table 1
Ionic radii r of sixfold coordinated R^{3+} ions; magnetic ordering temperatures T_c of $R_2Cu_2O_5$ compounds; splittings Δ of the Er^{3+} probe ground doublet

R	r(Å)	T_c (K)	Δ (cm^{-1})
In	0.80	26	19
Lu	0.85	20	20
Er	0.88	28	20
Y	0.89	14	18
Tb	0.92	21	19

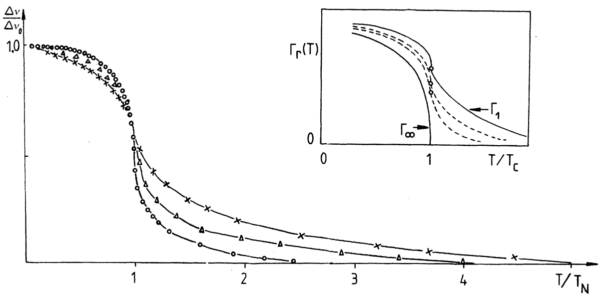

Fig. 4. Reduced splitting of the Er^{3+} probe IB line vs. reduced temperature plots for $Y_2Cu_2O_5$ (crosses), $Lu_2Cu_2O_5$ (triangles) and $Er_2Cu_2O_5$ (circles). $\Delta\nu_0\equiv\Delta\nu(T\rightarrow0)$. T_c—the temperature of the magnetic ordering. Inset: correlation functions $\Gamma_r(T)$ [15].

4. Spectral detection of magnetic ordering

The cuprates $R_2Cu_2O_5$ were thoroughly studied by different methods and therefore they were appropriate for the test of our spectral technique. The temperatures T_c of magnetic ordering of the $R_2Cu_2O_5$ cuprates found by us, from the points of inflections in the $\Delta\nu(T)$ curves, coincided satisfactorily with T_N determined by other methods [11]. Additional evidence of an ordering comes from the spectral line narrowing in the vicinity of T_c (see Fig. 3). We have found for the first time, magnetic ordering in Y_2BaCuO_5 [16], Lu_2BaCuO_5 [17], Nd_2BaCuO_5 [18], R_2BaNiO_5 with R=Nd-Ho, Tm, Lu [19–22] and have determined the temperatures T_c of the corresponding phase transitions.

It should be emphasized that the method of the rare-earth spectral probe is a microscopic one by its nature and, therefore, often gives a more deep insight into physical processes. As an example, our studies of the chain nickelate Er_2BaNiO_5 can be mentioned [19]. The spectrum of Er_2BaNiO_5 reveals a magnetic ordering at 34 K, in accordance with neutron scattering data [23]. The magnetic susceptibility $\chi(T)$ does not exhibit any anomaly at $T_N=$

34 K, but has a maximum at a considerably lower temperature $T_{max}=15$ K [23,19], which has been attributed in Ref. [23] to the antiferromagnetic ordering of the erbium subsystem. Our spectral measurements have shown that the maximum in $\chi(T)$ for Er_2BaNiO_5 does not correspond to any phase transition but is caused by the population changes within the ground Er^{3+} Kramers doublet split by the exchange interaction with an ordered nickel subsystem. In Er_2BaNiO_5, the magnetically ordered nickel subsystem polarizes the erbium subsystem and it becomes partially ordered. Subsequent ordering when lowering the temperature sets in gradually, due to emptying of the upper component of the Er^{3+} ground Kramers doublet split by the Ni–Er interaction. Only one magnetic phase transition takes place, both Ni and Er magnetic subsystems order simultaneously. We estimate an effective magnetic field experienced by the erbium ion to be $H_{eff}=2.8T$ at $T=0$.

As another example, it is interesting to refer to the history of the Y_2BaCuO_5 cuprate. This compound has drawn considerable attention just after the discovery of high-T_c superconductivity, as a component of Y-Ba-Cu-O superconducting ceramics, the so called ‘green phase’. The establishment of three-dimensional (3D) magnetic order in Y_2BaCuO_5 at about 16 K has been unambiguously revealed by our high-resolution spectral method of the RE probe [16] (as an illustration see Fig. 5) and, simultaneously and independently, by a μ^+ spin rotation [24]. It was confirmed later by another microscopic method of impurity probe in Mössbauer spectroscopy [25]. Magnetic susceptibility (χ) and specific heat macroscopic measurements failed to register this magnetic phase transition. A broad maximum around 30 K observed in the $\chi(T)$ curve for Y_2BaCuO_5, and at first erroneously attributed to the 3D magnetic ordering, has been shown to arise from low-dimensional magnetic correlations. There are isolated CuO_5 pyramids in the structure of Y_2BaCuO_5. Evidently, some low-dimensional Cu–O–O–Cu superexchange paths dominate there.

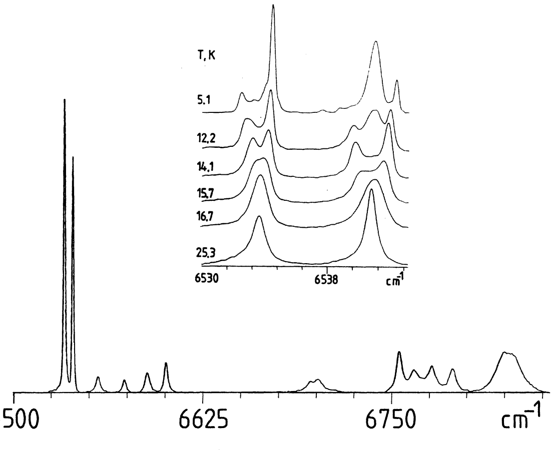

Fig. 5. The spectrum of Er^{3+} probe in Y_2BaCuO_5 at 25.3 K>T_N ($^4I_{15/2}\rightarrow{}^4I_{13/2}$ optical transition). Inset: two lowest frequency spectral lines originating from two nonequivalent positions of Er^{3+} in the structure, at different temperatures. The establishment of a magnetic ordering manifests itself by the splitting of the spectral lines.

Thus, high-resolution spectra of a RE ion, intrinsic or introduced as a probe, give the possibility of registering unambiguously magnetic phase transitions, even those not detectable by other methods, and to verify the interpretation of magnetic susceptibility (and specific heat) measurements.

5. Low-dimensional magnetism in $R_2Cu_2O_5$

For $T>T_c$, the splittings of spectral lines $\Delta\nu$ do not vanish—a ‘tail’ is observed due to short range order (see, e.g., Figs. 3 and 4). We have compared [26] the dependencies $\Delta\nu(T/T_c)$ for the Er^{3+} probe in several $R_2Cu_2O_5$ compounds with identical structures of copper magnetic moments μ_{Cu} but with different T_c temperatures. These compounds have already been listed in Table 1. The crystal structure of the $R_2Cu_2O_5$ cuprates is quasi-2D, namely, there are CuO *ab*-planes in them with the in-plane Cu–Cu distances considerably smaller than the interplane ones. These planes have no direct Cu–O–Cu interconnections through one oxygen. The Cu–Cu intraplane interactions must be alike in all the $R_2Cu_2O_5$ compounds possessing the same magnetic structure of an ordered copper subsystem and, therefore, short-range correlations due to the Cu–Cu intraplane interactions are likely to be observed up to the same temperature. Really, the tail of the residual splitting at $T>T_c$ extends till the same temperature (of ≈90 K) for all the compounds studied [26].

If the interplane interactions were absent, a long-range order would not set in, because a 2D Heisenberg system has no long-range order and Cu^{2+} in $R_2Cu_2O_5$ is, to a good approximation, the Heisenberg ion. For the $R_2Cu_2O_5$ cuprates with nonmagnetic Y and Lu ions, this interaction must depend mainly on the interplane distance which is smaller for $Lu_2Cu_2O_5$ than for $Y_2Cu_2O_5$ because of the smaller ionic radius of the Lu^{3+} ion (see Table 1). For $Er_2Cu_2O_5$ where the Er^{3+} ion has practically the same radius as the Y^{3+} ion, the interplane interaction must be greater than in $Y_2Cu_2O_5$ because this interaction goes through the magnetic Er^{3+} ions possessing large magnetic moments. Tb^{3+} in $Tb_2Cu_2O_5$ has almost the same magnetic moment as Er^{3+} in $Er_2Cu_2O_5$ but a greater ionic radius than Er^{3+}, that is why the interplane distance in $Tb_2Cu_2O_5$ is greater than in $Er_2Cu_2O_5$ and, as a result, the interplane interaction is smaller. These relative values of comparatively weak interactions between CuO planes in $R_2Cu_2O_5$ compounds determine the temperatures, T_c, of 3D ordering and, consequently, the lengths of the ‘tails’ in Fig. 4. One can say that the length of the ‘tail’ is the greater, the smaller is the ratio of the interplane interaction to the intraplane one, in other words, the closer is a system to a pure 2D one.

6. Spectral manifestation of ordering of the RE subsystem and spin–reorientation phase transitions in R_2BaMO_5 (M=Cu, Ni)

In some of the R_2BaMO_5 (M=Cu, Ni) compounds, an ordering of the RE subsystems occurs as a second phase transition at lower temperature. First, a d-magnetic subsystem orders into some magnetic mode imposed by the dominant d–d interactions. This mode may not be favorable for the RE subsystem, and though the latter gets polarized by a d–f interaction, anisotropic f–f (RE–RE) interactions may force it into another magnetic mode. In its turn, the ordered RE magnetic subsystem may cause, via anisotropic f–d interactions, a spin–reorientation phase transition inside the d-magnetic subsystem [27].

Such a sequence of magnetic phase transitions in Dy_2BaCuO_5 has been demonstrated by our spectral study of this compound [28]. It is worth making the following comment here. While the RE level splittings (and hence the shape of the spectrum) depend mainly on the d–f exchange interaction, the decisive contribution to the line-width comes, in many cases, from the magnetic dipole interactions with large unordered RE magnetic moments. In Dy_2BaCuO_5, copper magnetic subsystem orders at about 20 K via a second order phase transition. That causes the growing splitting of the Dy^{3+} levels and hence spectral lines which, however, remain relatively broad (see Fig. 6). An ordering of the Dy subsystem via a first-order phase transition at 11.26 K manifests itself by a sharp narrowing of the spectral lines (see the spectrum for $T=11.18$ K in Fig. 6). At 10.95 K, we observe one more different spectrum again, while both these spectra with interchanging intensities are present for intermediate temperatures ($T=11.10$ K in Fig. 6), in the course of a first order spin-reorientation transition within the Cu subsystem [28].

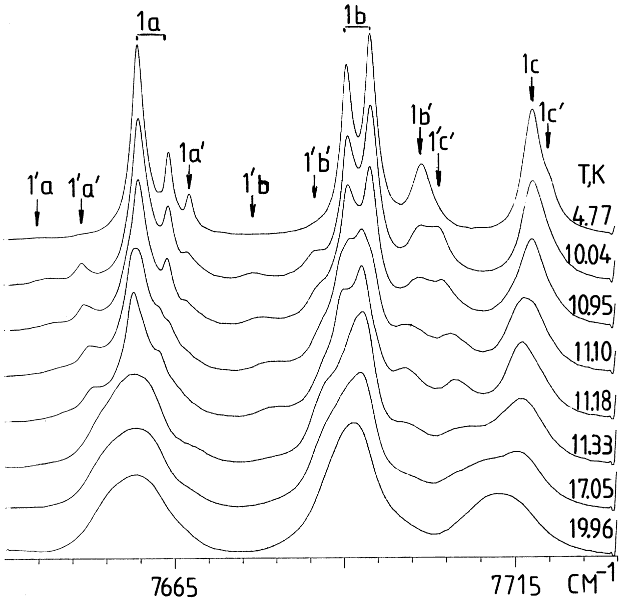

Fig. 6. The low frequency lines of the $^6H_{15/2}\rightarrow{}^6H_{9/2}+{}^6F_{11/2}$ transition in Dy_2BaCuO_5 at different temperatures.

We have detected spin–reorientation first-order phase transitions not known before also in Y_2BaCuO_5 [16,29], Lu_2BaCuO_5 [17] and Yb_2BaCuO_5 [17].

One more interesting example comes from our recent study of the chain nickelate Gd_2BaNiO_5 [22]. Magnetic measurements failed to find any spontaneous magnetic phase transition in it [19]. On the contrary, high-resolution optical spectra of the Er^{3+} probe present rich information about the magnetic properties of Gd_2BaNiO_5 as a function of temperature. Both Ni and Gd magnetic subsystems order simultaneously at 58±2 K to some high-temperature magnetic phase (HTP) which manifests itself by a considerable spectral line splitting and exists down to 32 K. Quite a different low-temperature magnetic phase (LTP), which is characterized by a single unshifted line, is observed below 21 K. The transition from the HTP to the LTP is complex and occurs through several intermediate magnetic structures [22].

7. Spectra of Er^{3+} probe and magnetic structure of the d-subsystem

In Section 3, we considered the example of the Er^{3+} probe in $R_2Cu_2O_5$ (R=Y, Lu, Er, Tb) and have shown that the splittings of the Er^{3+} levels are, mainly, due to the interaction with the d-magnetic subsystem. All these cuprates possess the same structure of copper magnetic moments in an ordered state, namely, ferromagnetically ordered ab-planes coupled antiferromagnetically one with the other, μ_{Cu} being aligned along the *b*-axis, and notwithstanding strongly different R^{3+} ions, the Er^{3+} probe ground-state splittings are close in all of them, being equal to 18–20 cm^{-1}. In $Tm_2Cu_2O_5$, where the same copper magnetic planes exist but μ_{Cu} is aligned along the *a*-axis [13], the Er^{3+} ground-state splitting is about 2.0 cm^{-1}, an order of magnitude smaller than in $R_2Cu_2O_5$ with R=Y, Lu, Er, Tb. It follows from this result that Er–Cu interactions are highly anisotropic.

On these grounds, we have made a choice [10,11] between two contradictory interpretations of neutron scattering data for $Yb_2Cu_2O_5$. The spectrum of the Er^{3+} probe in $Yb_2Cu_2O_5$ closely resembles that in $Tm_2Cu_2O_5$ (where $\mu_{Cu}\|a$) and differs significantly from the spectrum of $Er_2Cu_2O_5$ (where $\mu_{Cu}\|b$). In our opinion, this favours the alignment of the copper magnetic moments in $Yb_2Cu_2O_5$ along the *a*-axis, in accordance with Ref. [30], rather than along the *b*-axis as has been proposed in Ref. [31]. In $Yb_2Cu_2O_5$, each spectral component is split into doublet, reflecting doubled-spectral positions in a doubled magnetic cell, in comparison with $Tm_2Cu_2O_5$ [11]. We speculate that in $In_2Cu_2O_5$, where no neutron scattering data exist, μ_{Cu} must be aligned along the *b*-axis, on the grounds of a close similarity between the spectra and level splittings of the Er^{3+} probe in $In_2Cu_2O_5$ and in $R_2Cu_2O_5$ with R=Er, Lu, Tb, where $\mu_{Cu} \| b$ (see Table 1) [32].

A systematic study of the spectra of Er^{3+} in the 'green phases' R_2BaCuO_5 is now in progress. We have already published some of our results [17,33].

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