Variable valence and ESR of yttrium ceramics

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Expressions are derived for the spin susceptability, the width of the ESR line, and the shift of the resonant frequency of paramagnetic ions in a variable-valence state. The theoretical temperature dependence of the parameters of the ESR spectrum of nonsuperconducting phases of ceramic $YBa_2Cu_3O_x$ agrees with experimental data. It is suggested that, as the oxygen content in $YBa_2Cu_3O_x$ increases from 6.1, the valence of the copper ions in Cu1 sites decreases, reaching values $\lesssim 1.6$–1.7 for the superconducting phases of this ceramic. The same effect would explain the sharp decrease in the intensity of the ESR signal in superconducting $YBa_2Cu_3O_x$ samples.

Research on ESR in metal-oxide ceramics has shown that the spin paramagnetism of copper is greatly suppressed in La_2CuO_4 and $La_{1.8}Sr_{0.2}O_{4\quad x}$ (Ref. 1), and the ESR signals correspond to only a few percent of the Cu atoms in a net-spin state. The published ESR data on the yttrium ceramics are extremely contradictory.[1,2] The absence of any significant changes in the ESR spectra of these compounds near the superconducting transition temperature has allowed several authors (e.g., Romanyu *et al.*[3] and Rettori *et al.*[4]) to suggest that the magnetic resonance arises predominantly in phases which are not responsible for the superconductivity. In the superconducting phases, in contrast, the copper ions are believed to be in a spin-zero Cu^+ state (this is apparently the most likely situation for Cu1 sites) or in a state with a higher valence (many pieces of evidence indicate that this is the case for CuO_2 planes). There would thus be a pronounced broadening of the ESR line, because of a strong exchange interaction of magnetic moments of copper with each other and with holes. In our opinion, certain questions pertaining to studies of the ESR in the superconducting phases of the

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yttrium ceramics—questions which seem to be causing difficulties— can be solved by a comprehensive analysis of the existing results on the ESR in the nonsuperconducting phases of these compounds. For example, the fractional-power law which was found for the temperature dependence of the integral ESR intensity in Ref. 3, and which arises, according to Ref. 2, from Cul ion [$\chi(T) \sim T^{-\alpha}$ with $\alpha = 0.95$, 0.82, and 0.71 for $x = 6.1$, 6.15, and 6.28 in $YBa_2Cu_3O_x$], combined with the circumstance that an ESR is not observed in the superconducting phase, with $x > 6.5$, can apparently be linked with the presence of Cu^{m+1} copper ions in a state with a variable valence m. This valence would decrease from $m \sim 2$ as the oxygen concentration increases from $x \sim 6.1$. This suggestion also finds support in the results of a study[5] of the Mössbauer effect in $YBa_2Cu_3O_{6+\delta}$. It was shown there that the charge exchange $2Cu^{1,5+} \rightleftarrows Cu^{+} + Cu^{2+}$ occurs in the superconducting phase of the composition $YBa_2Cu_2^2 + 2Cu^{1,5} + 1O_6^{2-}O^{-}$, with an exchange time shorter than the time scale of a Mössbauer experiment with ^{57}Fe: $\sim 10^{-8}$ s. An intermediate valence of copper in the 1-2-3 compounds was also reported in Refs. 6 and 7.

To find the dynamic susceptibility of localized spins of Cul ions with a variable valence, we start from the Hamiltonian

$$\hat{\mathcal{H}} = \sum_{k\sigma} \epsilon_{k\sigma} c_{k\sigma}^{+} c_{k\sigma} + \sum_{i\sigma} \epsilon_{\sigma}^{2+} d_{i\sigma}^{+} d_{i\sigma} + \sum \epsilon^{+} e_i^{+} e_i$$

$$+\lambda \sum_i \left(e_i^{+} e_i + \sum_\sigma d_{i\sigma}^{+} d_{i\sigma} - 1\right) + V_0 \sum_{ik\sigma} [e_i d_{i\sigma}^{+} c_{k\sigma} + \text{c.c.}].$$

Here e_i^{+} and $d_{i\sigma}^{+}$ are creation operators for Cu^{+} and Cu^{2+} valence states, with energies ϵ^{+} and $\epsilon_{\sigma}^{2+} = \epsilon^{2+} + \sigma(\omega_d/2)$; $\omega_d = g_d \mu_B H_0$; g_d is the g-factor of the Cu^{2+} ion; μ_B is the Bohr magneton; H_0 is the external magnetic field, $c_{k\sigma}^{+}$ and $c_{k\sigma}$ are field operators of the band electrons (or holes), with an energy $\epsilon_{k\sigma}$; V_0 is the hybridization energy of the band and localized electrons at the ith copper ion; and λ is an undetermined Lagrange multiplier.[8] In linear-response theory, the dynamic susceptibility is given in terms of the two-particle Green's function of the magnetic-moment operators of the copper ions:

$$\chi^{+-}(\omega_0) = < T_\tau M^{+}(\tau) M^{-}(\tau') >_{\omega_0}; \quad M^{\pm} = \frac{1}{\sqrt{2}} g_d \mu_B \sum_i d_{i\pm}^{+} d_{i\mp}. \tag{1}$$

Calculations of dynamic response (1) with the help of temperature Green's functions and a Feynman-diagram technique developed for similar calculations in Refs. 9–11 lead to the following result in the high-temperature approximation ($T \gg \omega_d, \omega_0$):

$$\chi^{+-}(\omega_0) = \frac{\omega_d \chi(T)}{\omega_d(1+k) - \omega_0 + i\frac{1}{T_1}}; \quad \chi(T) = \chi(T_0) \frac{T_0}{T} \frac{2}{\gamma^{T_0/T} + 2}; \tag{2}$$

$$k = k_0\left(1 + B\frac{T_0}{D}\right); \quad \frac{1}{T_1} = \frac{1}{T_1^0}\left(1 + B\frac{T_0}{\Gamma}\right); \quad k_0 = \frac{g_c}{g_d} \rho J_0;$$

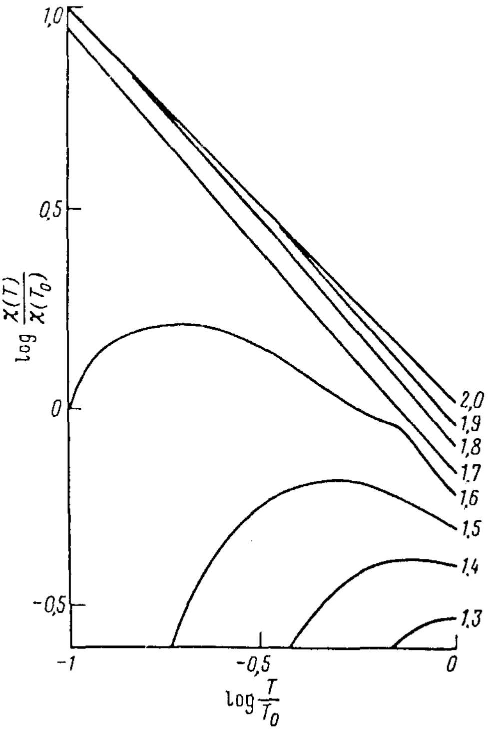

FIG. 1. Temperature dependence of the spin susceptibility, in logarithmic scale.

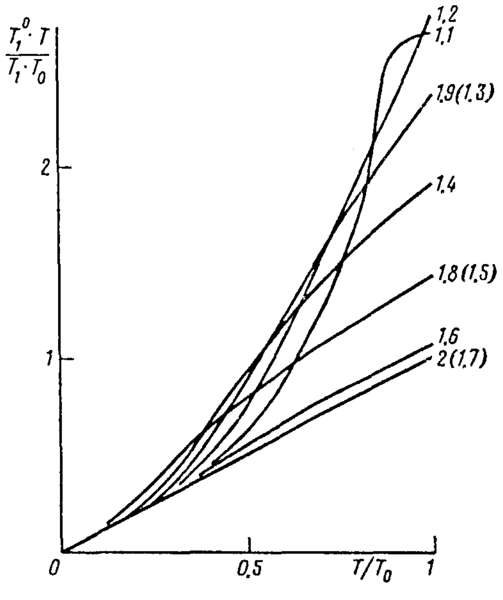

FIG. 2. Temperature dependence of the relaxation rate determined by $T_0/G = 2$.

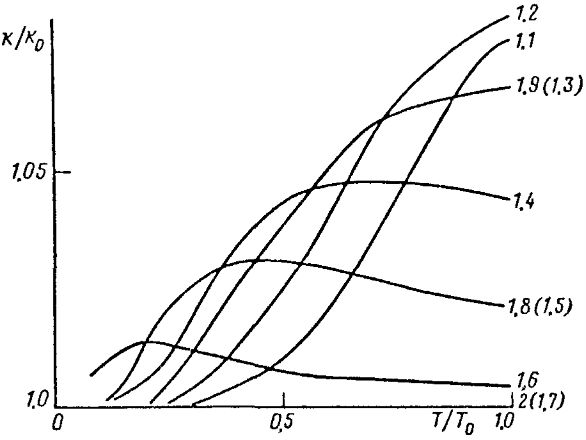

FIG. 3. Temperature dependence of the shift of the resonance frequency, determined at $T_0/D = 0.1$.

$$\frac{1}{T_0} = \pi\rho^2 J_0^2 T; \quad \chi(T_0) = \frac{c g_d^2 \mu_B^2}{4T_0}; \quad J_0 = \frac{V_0^2}{\epsilon^{2+} - \epsilon^{+}};$$

$$B = 2\frac{T_0}{T}\alpha^2 \frac{\gamma^{T_0/T}}{(\gamma^{T_0/T}+1)^2}; \quad \alpha = \frac{\epsilon^{2+} - \epsilon^{+}}{T_0}; \quad \gamma = \exp\alpha.$$

Here c is the concentration of CuI copper ions; D is the half-width of the conduction band; Γ is the width of the localized level of the Cu^{2+} ion; g_e is the g-factor of the band quasiparticles, with a state density ρ at the Fermi surface; and T_0 is the temperature at which the CuI copper ion is "tested" for valence. At this temperature, the valence is given by $m = (\gamma + 4)/(\gamma + 2)$. Figures 1–3 show the temperature dependence of the ESR parameters found from (2). The values of the valence m at $T = T_0$ are shown beside the corresponding curves. The temperature dependence $\chi(T)$ in Fig. 1 shows that for $1.65 \lesssim m \leqslant 2$ we see an $\chi(T) \sim T^{-\alpha}$ dependence with $0.7 \lesssim \alpha < 1.0$. At $m < 1.65$, the quantity $\chi(T)$ and thus the intensity of the ESR signal fall off sharply with decreasing temperature. This behavior of $\chi(T)$ leads to the conclusion that the valence of the Cu^{m+}I ions in the superconducting phases of the 1-2-3 ceramics is less than 1.65–1.7, while in the normal phases (with a lower oxygen content) this value changes from 1.65 to 2. This conclusion is supported by the agreement between the temperature dependence of the linewidth (Fig. 2) and that of the shift of the resonance frequency (Fig. 3), determined from (2) and the experimental curves of Refs. 2 and 3. Values $m \sim 1.65$–1.7 are also indicated by the results of the Mössbauer study in Ref. 5, where it was reported that 30% of the ions are Cu^{+}I ions, and 70% are Cu^{2+}I ions, in the superconducting phase of $YBa_2Cu_3O_{6+\delta}$. The curves in Figs. 2 and 3 lead to certain conclusions regarding the transport of magnetic excitations in variable-valence compounds. For example, it is interesting to note that in the interval $m \sim 1.6$–1.7, in which the superconductivity arises, according to the present understanding, the relaxation rate and frequency shift are at their smallest. The most effective magnetic relaxation, which occurs at slight deviations of the valence from an integer value, is apparently linked with the correlation observed experimentally between the valence and the coefficient κ in the temperature dependence of the specific heat ($c_V = \kappa T$) for several compounds. For example, the highest value of κ is observed in compounds in which the valence tends toward an integer value. In $CeAl_3$, for example, the valence of cerium is $m_{Ce} \sim 3.03$, and the value of κ is 1100 mJ/K^2 (Ref. 12). In $CuRu_2$, on the other hand, with $m_{Cu} \sim 3.3$ (Ref. 13), we have $\kappa \approx 23$ mJ/K^2(Ref. 12).

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