

Electronic structure of Eu in the high- T_c superconductor $\text{Ba}_2\text{EuCu}_3\text{O}_{7.1}$

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The Mössbauer effect of the 22-keV γ line of ^{151}Eu has been employed to study the electronic configuration of Eu ions in the high- T_c superconducting material $\text{Ba}_2\text{EuCu}_3\text{O}_{7.1}$. The isomer shift is constant as a function of temperature and shows that Eu is present as $\text{Eu}^{3+}(4f^6)$.

Since the announcement of high- T_c superconductivity (near 30 K) in the La-Ba-Cu-O chemical system,¹ the search for other high-temperature superconductors has increased tremendously. Further study has demonstrated that bulk superconductivity occurs in a quaternary-phase $\text{La}_{1.8}\text{Ba}_{0.2}\text{CuO}_4$ with a K_2NiF_4 -type structure.² The identification of this phase quickly led to the chemically substituted phase $\text{La}_{1.8}\text{Sr}_{0.2}\text{CuO}_4$ which has a T_c near 40 K.³⁻⁶ More recently, superconductivity at temperatures of 90–95 K in the Y-Ba-Cu-O chemical system was reported by Wu *et al.*⁷ The very high T_c 's in the Y-Ba-Cu-O system were obtained in a multiphase material of composition $\text{Y}_{1.2}\text{Ba}_{0.8}\text{CuO}_{4-y}$.⁷ The superconductivity phase in the Y-Ba-Cu-O system was subsequently identified by analysis as $\text{Ba}_2\text{YCu}_3\text{O}_{6.9}$.⁸ The structure was found to be a previously unknown distorted, oxygen-deficient perovskite.⁹⁻¹¹ Several new superconducting cuprate perovskites with other rare earths substituted for Y have been prepared¹²⁻¹⁴ and found to have T_c 's comparable to the yttrium compound. Some of these rare-earth ions, such as Eu, Sm, and Yb can be divalent or trivalent. Since there is little effect on T_c from substitution with other rare earths, even for Gd, it is likely that they are all trivalent and do not contribute substantially to the conduction band.¹²⁻¹⁴ Unambiguous assignment of the electronic state of these rare earths is crucial to interpretation of physical property measurements and theoretical modeling.

In this report we address the question of the valence of Eu in its compound using ^{151}Eu Mössbauer data. These data establish unambiguously that the Eu is trivalent with the electronic configuration $4f^6$. The Mössbauer "isomer shift" measures the density of s electrons at the Eu nucleus. For rare-earth ions, an increase in the number of $4f$ electrons results in increased shielding of the s electrons (especially the two $5s$ electrons). The shielding effect is much larger than the direct change in s density obtained by a change in $6s$ configuration. The measured isomer shift provides a direct measurement of the number of $4f$ electrons. Thus, the Mössbauer effect is an ideal tool to investigate the valence state of Eu in this high- T_c superconducting material.

The Mössbauer spectra at various temperatures were obtained in transmission geometry using a standard constant acceleration spectrometer. The source was ^{151}Sm in a SmF_3 matrix, and the γ rays were detected by a silicon detector. Spectra as a function of temperature are shown

in Fig. 1. A single resonance absorption line was observed. The isomer shift was evaluated by least-squares fitting a single Lorentzian to the data. The isomer shift as a function of temperature is shown in Fig. 2, along with "calibration" results for selected Eu^{3+} and Eu^{2+} compounds.¹⁵ Comparison of the results with those for Eu in known valence states shows that the Mössbauer line falls at the $\text{Eu}^{3+}(4f^6)$ valence state. The Eu ions remain in the same valence state below and above the superconducting state, $T_c = 94$ K.

The isomer shift of Eu in the compound analyzed to be $\text{Ba}_2\text{EuCu}_3\text{O}_{7.1}$ looks very much like trivalent Eu in non-

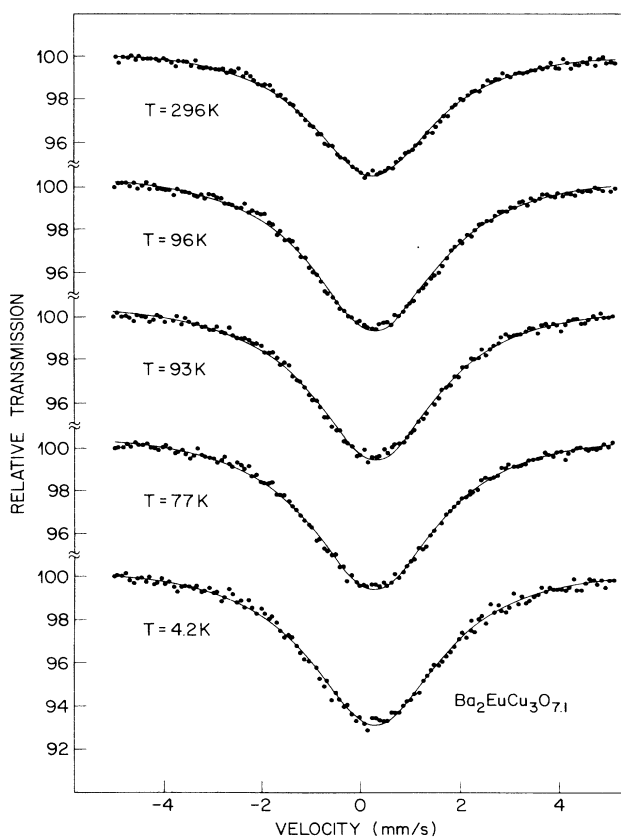


FIG. 1. Mössbauer absorption spectra of the 22-keV resonance in ^{151}Eu of $\text{Ba}_2\text{EuCu}_3\text{O}_{7.1}$ as a function of temperature. The solid line is a Lorentzian least-squares fit to the data.

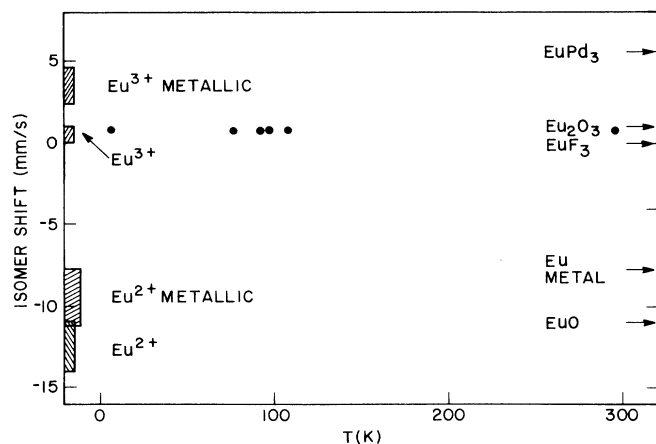


FIG. 2. Isomer shift (corresponding to s -electron density at the ^{151}Eu nucleus) vs temperature for $\text{Ba}_2\text{EuCu}_3\text{O}_{7.1}$. Typical values for selected ionic and metallic Eu^{2+} and Eu^{3+} compounds are also shown. The data have not been corrected for second-order Doppler shift, which is temperature dependent. The high effective Debye temperature (Ref. 16) of this material (350 K) should make this correction small below 300 K.

conducting oxides, such as Eu_2O_3 , and suggests that Eu plays a minor role in conductivity. The extensive substitutions possible in the rare-earth site^{12,14} with little effect on T_c are also indicative of the subordinate role of the rare earth in the electronic properties. This is consistent with band-structure calculations.^{17,18}

Even though the rare earth does not strongly affect the electronic properties, they are crucial to formation of the structure because of their size and charge. The trivalent charge on the rare-earth ion in combination with a divalent charge for Ba and the observed oxygen stoichiometry results in an appropriate copper oxidation state (~ 2.4) for metallic conductivity.

We have established unambiguously that Eu is trivalent and does not strongly affect the electronic properties of the $\text{Ba}_2\text{EuCu}_3\text{O}_{7.1}$. The understanding of the electronic structure is a major step in explaining the electronic properties of the defect perovskites cuprate superconductors.

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