
DEHYBRIDIZATION IN CUPRATES

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The electronic structure of ScCu_2Si_2 , LaCu_2Si_2 , EuCu_2Si_2 and YbCu_2Si_2 intermetallic compounds was studied by X-ray emission spectroscopy. The evidence is presented that the dehybridization effect is inherent not only in the ternary cuprates of the CeGa_2Al_2 structural type, but also in the compounds of other structural types. This fact implies a large-scale prevalence of the dehybridization phenomenon, which, in particular, is characteristic of the high-temperature superconductors.

The observation of the dehybridization phenomenon was first reported in 1981 for EuCu_2Si_2 compound [1, 2]. Later on, a similar effect was revealed in CeCu_2Si_2 [3, 4], LaCu_2Si_2 , YbCu_2Si_2 , and ScCu_2Si_2 [5] intermetallic compounds. The essence of the observed phenomenon is thought to originate from the specific features of the electron band structure of such compounds and will become clear from what follows.

Fig. 1 shows the electron band diagrams for ScCu_2Si_2 , LaCu_2Si_2 , EuCu_2Si_2 and YbCu_2Si_2 compounds. Strongly pronounced anomalies, which represent itself in a bifurcation of $\text{Si}K\beta_{1,x}$ bands, are characteristic of the superpositions obtained. What is more, for ScCu_2Si_2 and LaCu_2Si_2 compounds, the bifurcation is also observed for $L_{2,3}$ bands which reflect a distribution of the filled electron states of the $s(d)$ -type symmetry in silicon. However, for Eu- and Yb-containing compounds, the $L_{2,3}$ band bifurcation is not observed, although the center of the band area shifts towards a low-energy side, and the horizontal high-energy plateaus denoted as E and C' in Fig. 1 lose their peculiar relief structure (such the structure, for instance, is inherent to the compounds of RM_2Si_2 ($M \neq \text{Cu}$) series).

For the ternary cuprates, the double-peak structure of $\text{Si}K\beta_{1,x}$ bands can be explained by a fact that the copper $3d$ shell ($L\alpha_{1,2}$ band) splits $\text{Si} 3p$ states ($K\beta_{1,x}$ band), leading to the formation of two maxima (denoted as A and C in Fig. 1). We interpret the splitting of such a kind as a dehybridization effect of $(3d-3p)$ -type. At the same time, the splitting of $\text{Si}L_{2,3}$ bands in Eu- and Yb-containing compounds, as well as the shift of $\text{Si} s(d)$ states out of the zone of the energy

localization of $\text{Cu}3d$ states in EuCu_2Si_2 and YbCu_2Si_2 intermetallic compounds enables us to speak about the dehybridization of $(3d-3s)$ -type.

Dehybridization processes of the above types originate from a high-energy steadiness of $\text{Cu}3d$ shell which acquires atomic-like features in ternary cuprates with an energy shift of about 3 eV towards the low-energy side, relative to the energy position of $3d$ shell in similar compounds containing Fe, Co, or Ni. Fig. 2 shows the superpositions of the emission spectra for the compounds of RNi_2Si_2 series and demonstrates more clearly a difference in the electron band structure between the ternary cuprates and other compounds of RM_2Si_2 ($M \neq \text{Cu}$) series. RNi_2Si_2 compounds may be considered as the prototypes of the Cu-containing ones, since they differ only in a type of $3d$ metal. Thus, the variations of the electron band structure arising upon the $\text{RNi}_2\text{Si}_2 \leftrightarrow \text{RCu}_2\text{Si}_2$ transition are caused by the $\text{Ni} \leftrightarrow \text{Cu}$ substitution.

It follows from the above arguments that a fundamental factor, which underlies the changes in the electron band structure observed upon the transition from RNi_2Si_2 and RCu_2Si_2 compounds, is the electron structure of $\text{Ni}(3d^9 4s^1)$ and $\text{Cu}(3d^{10} 4s^2)$ atoms. The peculiar feature of the Cu-containing compounds is thought to be a high energy steadiness of $3d$ shell. The manifestation of this energy steadiness is the 2.5 eV energy shift towards the low-energy side, characteristic of $\text{Cu}3d$ states ($L\alpha_{1,2}$ band) in RCu_2Si_2 compounds as compared with $\text{Ni}3d$ states in RNi_2Si_2 compounds (see Figs. 1 and 2). In addition, one can observe the minima in the silicon emission spectra, whose energy position coincides with the maxima of the $\text{Cu}L\alpha_{1,2}$ emission bands, with the latter reflecting the distribution of $3d$ states.

A comparative analysis of the compounds of both series, RNi_2Si_2 and RCu_2Si_2 ($R = \text{Sc, La, Eu, Yb}$), reveals essential differences in the energy distribution of their electron states. It is worth noting that, for the isostructural compounds of RM_2Si_2 series where M is $3d$ metal except for Cu, the features of the distribution of the electron states of the valence band are rather similar

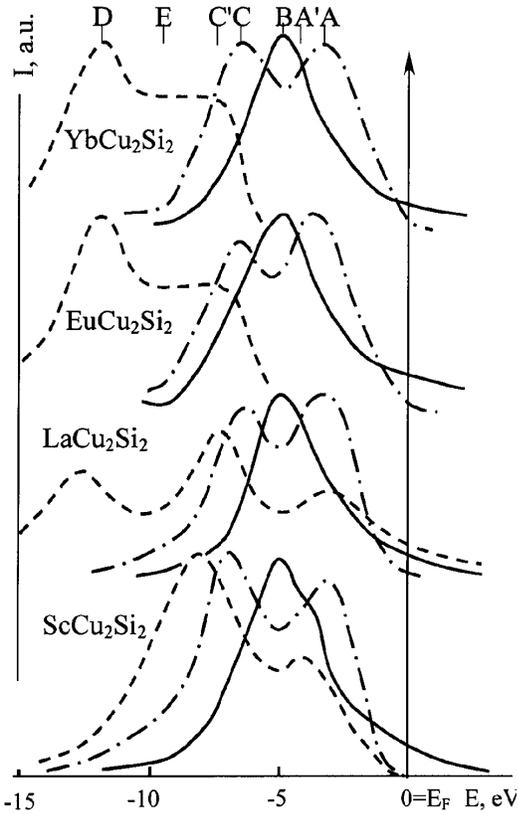


Fig. 1. Dehybridization phenomenon in the compounds of RCu_2Si_2 series: $CuL\alpha_{1,2}$ band (solid line), $SiK\beta_{1,x}$ band (dash-dotted line), and $SiL_{2,3}$ band (dashed line)

to each other, with differences occurring only in insignificant details [1]. A sharp change appears only upon the transition to cuprate compounds.

It turns out that not only Si (spd) states are split under the influence of the energetically steady $3d$ shell of copper. Such an effect is also characteristic of the $4f$ states of R elements for the case of $EuCu_2Si_2$ and $YbCu_2Si_2$ ternary cuprates. The evidence for this is presented in Fig. 3 which compares the photoelectron spectra (PES) for $LaCu_2Si_2$ and $EuCu_2Si_2$ compounds. An essential difference between these spectra consists in an intensive peak on the Fermi level, which is observed in the PES of $EuCu_2Si_2$ intermetallic compound (denoted as A in Fig. 3) but absent in that of $LaCu_2Si_2$ (Fig. 3, d). It is worth noting that the PES of the La-containing compound does not reflect those peculiarities of the electron structure, which are evident in $SiK\beta_{1,x}$ emission spectra (A' and C in Fig. 1) and are a result of the dehybridization effect of $(3d-3p)$ -type.

The formation of the intensive peak of the density of electron states, $g(E)$, observed in $EuCu_2Si_2$ compound

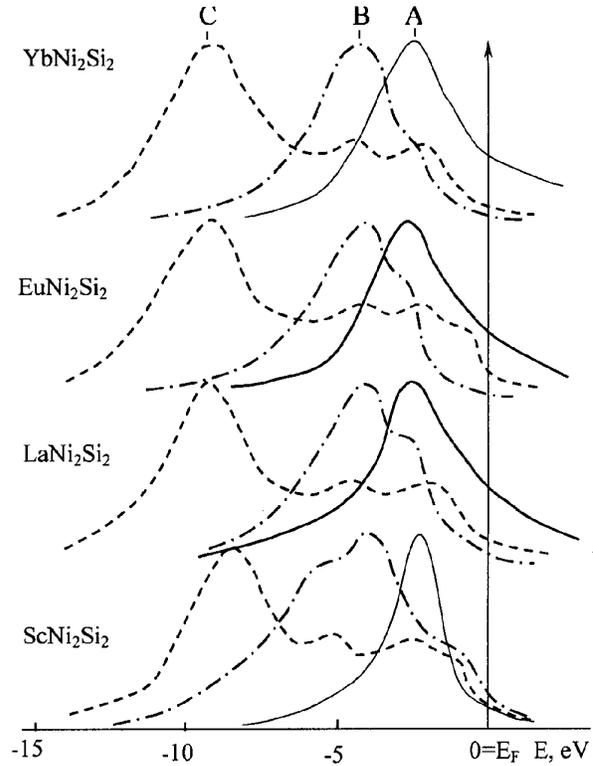


Fig. 2. X-ray emission spectra for the compounds of RNi_2Si_2 series: $NiL\alpha_{1,2}$ (solid line), $SiK\beta_{1,x}$ (dash-dotted line), $SiL_{2,3}$ (dashed line)

(the so-called Abrikosov—Suhl resonance) is caused by the approach of the $Eu4f$ states, which are activated by the compact $3d$ shell of copper, to the Fermi level. Thus, in this case, the dehybridization of $(3d-4f)$ -type occurs, whereas Fig. 1 illustrates similar effects of $(3d-3s)$ -character.

The approach of the activated $Eu4f$ states with uncompensated magnetic moments to the Fermi level leads to the formation of singlet bonding states of the $\langle f \uparrow | s \downarrow \rangle$ type, and this, in turn, results in the formation of a peak of the density of electron states, which is classified as the Abrikosov — Suhl resonance [6]. In this case, as was shown in [7], the wave function of the ground state is of a singlet Kondo character and can be described as

$$\Psi_{\text{Kondo}} = \frac{1}{\sqrt{2}}(\chi_{\uparrow}\psi_{\uparrow} - \chi_{\downarrow}\psi_{\downarrow}), \quad (1)$$

where χ_{\uparrow} , χ_{\downarrow} are wave functions of the quasiautomatic type which, for the case under consideration, are of $4f$ -symmetry, and ψ_{\uparrow} , ψ_{\downarrow} are the wave functions of conduction electrons.

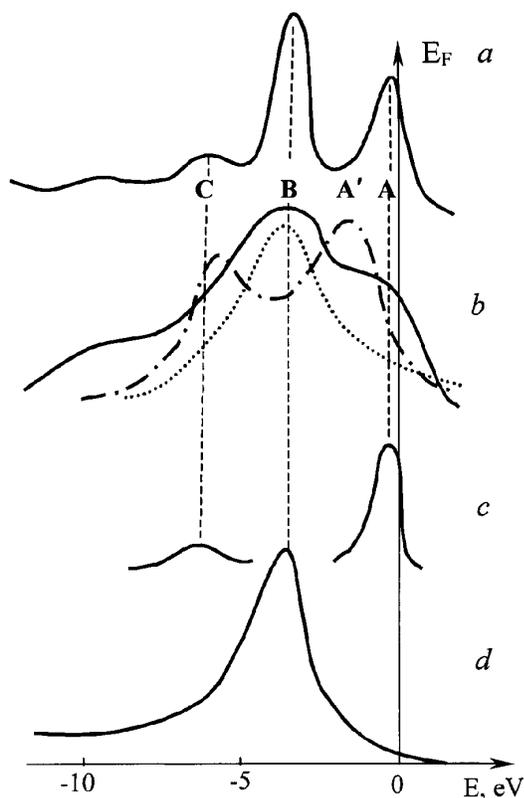


Fig. 3. Spectroscopic manifestation of the dehybridization phenomenon in EuCu_2Si_2 (a – c) and LaCu_2Si_2 (d) compounds. a, d — photoelectron spectra, b — emission spectra: $\text{CuK}\beta_{2,5}$ (solid line) and $\text{SiK}\alpha$ (dotted line), c — $4f$ -states

Thus, for EuCu_2Si_2 compound, an increase in the density of electron states on the Fermi level is predominantly caused by the $\text{Eu}4f\text{—Cu}3d$ dehybridization effect. Therefore, both the phenomena, the dehybridization effect of the given type and the Abrikosov—Suhl resonance, are interdependent.

It was shown above that all the ternary cuprates considered here are isostructural homologs which belong to the same structural type, namely to that of CeGa_2Al_2 [8]. It is worth noting that the electron band structure of ScCuSi compound [9] has also peculiar features characteristic of RCu_2Si_2 ($\text{R} = \text{Sc}, \text{La}, \text{Eu}, \text{Yb}$) homology series. In this respect, it is important to mention that ScCuSi intermetallic compound belongs to the ZrNiAl structural type [8] which is a superstructure to the Fe_2P structural type. The differences between CeGa_2Al_2 ($I4/mmm$ space group) and ZrNiAl ($P\bar{6}, 2m$ space group) structural types are described in [8] in detail.

The presence of the dehybridization features in the compounds belonging to various structural types

implies that the above phenomenon is of a general character and inherent not only to the cuprates of the R—Cu—Si system, but also to any compounds, alloys, solid solutions, or oxides which contain copper. In this respect, it is expedient to note that, without any exception, all high-temperature superconductors (HTSC) are cuprates: $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ ($T_c=40$ K), $(\text{Nd,Ce,Sr})_2\text{CuO}_4$ ($T_c=28$ K), $(\text{Nd}_{2-x}\text{Ce}_x)\text{CuO}_4$ ($T_c=24$ K), $\text{YBa}_2\text{Cu}_3\text{O}_7$ ($T_c=90$ K), $\text{YBa}_2\text{Cu}_4\text{O}_8$ ($T_c=80$ K), $\text{Y}_2\text{Ba}_4\text{Cu}_7\text{O}_{14}$ ($T_c=40$ K), $\text{Pb}_2\text{Sr}_2\text{NdCu}_3\text{O}_8$ ($T_c=70$ K), $\text{TlBa}_2\text{CaCu}_2\text{O}_7$ ($T_c=103$ K), $\text{TlBa}_2\text{Ca}_2\text{Cu}_3\text{O}_9$ ($T_c=120$ K), $\text{Tl}_2\text{Ba}_2\text{CuO}_6$ ($T_c=90$ K), $\text{Tl}_2\text{Ba}_2\text{CaCu}_2\text{O}_8$ ($T_c=112$ K), $\text{Tl}_2\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$ ($T_c=125$ K) [10]. Here, T_c is the transition temperature to a superconducting state.

Now, it is reasonable to assume that Cu_nO_m atomic structural groups, which with various combinations of the $\{n, m\}$ indices are present in all the above HTSC compounds, play an exceptional role in the formation of the superconducting properties. In fact, the detailed neutron as well as X-ray diffraction studies [10] have shown that the characteristic feature of the crystalline structure of $\text{YBa}_2\text{Cu}_3\text{O}_7$ compound is the alternation of the layers of pyramids consisting of oxygen anions and copper cations, with the latter located at the center of a pyramid base. The average distance from a copper cation to oxygen anions located in the pyramid base equals 1.945 Å, whereas that to the O^{2-} anion placed in the pyramid vertex is 2.298 Å. The reduced Cu—O distances are the indication of a strong interaction between atoms. A calculation of the sum of Cu^{3+} and O^{2-} ionic radii gives: $r_{\text{O}^{2-}} + r_{\text{Cu}^{3+}} \approx 1.360 + 0.580 \approx 1.940$ Å, which well coincides with the above value of the interatomic distance. The valence state of Cu ions ($3+$) is indicative of the participation of copper $3d$ electrons in the formation of Cu—O bonds. The break of the collapsed $\text{Cu}3d$ states gives rise to the formation of the hybrid bonding orbitals of ($\text{Cu}3d\text{—O}2p$)-type. It is the energy steadiness of the $\text{Cu}3d$ states that leads to a compactness and collapsed character of Cu—O bonds. In turn, the energetically stable Cu—O hybrid orbitals play a specific role which is similar to that played by the copper $3d$ shell in R—Cu—Si compounds. Thus, it is a steadiness of Cu—O bonds that is the leading factor which gives rise to the splitting of the valence band in HTSC. What is more, the splitting of the HTSC electron states by the Cu—O bonding orbitals can lead to a resonant increase in the electron density of states in the vicinity of the Fermi level, $g(E_F)$. In fact, for $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$ compound, the electron specific heat coefficient γ ($\gamma \sim g(E_F)$) reaches $(5 \div 8)$ $\text{mJ}/(\text{mole}\cdot\text{K}^2)$, the value being almost by one order higher than that characteristic of pure copper.

A similar situation is also observed in other HTSC [10].

The resonant increase in the density of filled electron states at $E = E_F$ essentially affects the value of the transition temperature to a superconducting state, T_c . The point is that the expression for the T_c value obtained in the BCS theory [11],

$$kT = 1.14\omega_c \exp \left[-\frac{1}{N(0)V} \right], \quad (2)$$

is only valid under the condition that $g(E_F \pm k\Theta_D)$ is constant. It is fulfillment of this condition that allows reducing the problem of the appearance of attraction between the electrons of a superconducting (Cooper) pair, which occurs due to the virtual phonon exchange, to a two-dimensional task. For the potential well obtained, the bonding energy is a function of the parameters of the well, and, owing to this, the exponential function appears in (2). It is in systems with the resonant increase of the density of electron states that both relation (2) and the above condition, $g(E_F \pm k\Theta_D) = \text{const}$, become invalid. In copper-containing compounds, one of the likely reasons for such an increase may be the dehybridization of the $(\text{Cu}3d - \text{O}2p)$ -orbitals.

The dehybridization effect revealed in cuprates can be inherent, in full measure, to the Ag- and Au-containing compounds, since, just as copper, these metals have energetically steady electron configurations, $4d^{10}$ and $5d^{10}$, respectively. Therefore, high temperatures of the transition to the superconducting state are expected, in particular, in the oxide compounds of the following systems: Y—Ba—Ag—O, Tl—Ba—Ca—Ag—O, Tl—Ba—Ag—O, as well as Y—Ba—Au—O, Tl—Ba—Ca—Au—O, Tl—Ba—Au—O.

HTSC with T_c in the temperature range 90—125 K, in which Cu is substituted by Ag or Au, may be considered as the prototypes of these hypothetical systems of compounds.

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ДЕГІБРИДИЗАЦІЯ В КУПРАТАХ

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Резюме

Методом рентгенівської емісійної спектроскопії досліджено електронну структуру інтерметалічних сполук ScCu_2Si_2 , LaCu_2Si_2 , EuCu_2Si_2 та YbCu_2Si_2 . Показано, що дегібридаційний ефект проявляється не тільки в тернарних купратах структурного типу CeAl_2Ga_2 , а також в сполуках інших структурних типів. Відмічена особливість є свідченням масштабності явища дегібридації, яке проявляється, зокрема, у високотемпературних надпровідниках.