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Department of Solid State Physics, Moscow State University[1]) *(a)*,
Laboratory of Surface and Interface Physics, Eotvos University, Budapest[2]) *(b)*, *and*
Department of Metallurgy, University of Strathclyde[3]) *(c)*

The Effect of the Electronic Density of States on the Stability of Dilute Cu-Based Alloys with 3d-Metals

By

V. S. STEPANYUK(a), A. SZASZ (b), A. A. KATSNELSON (a), A. V. KOZLOV (a), and A. HENDRY (c)

The electronic properties of dilute Cu-based alloys are calculated by the method of linear augmented plane waves. The results are correlating with the stability of these alloys, and giving possibility to approximate the solubility of the alloying elements in Cu. A successful comparison with the experiments is given.

Die elektronischen Eigenschaften von verdünnten Cu-Legierungen werden mit Hilfe der linearen APW-Methode berechnet. Die Ergebnisse korrelieren mit der Stabilität der Legierungen und ermöglichen es, die Löslichkeit des Legierungselements in Cu zu approximieren. Es wird ein sorgfältiger Vergleich mit dem Experiment durchgeführt.

1. Introduction

In general the imperfections in metals play an important role and influence many physical properties such as conductivity, thermopower, optical properties, and so on. The changes are conspicuous particularly when alloying with transition metal impurites. For example, when a transition metal is added to the host metal, additional peaks can appear in the absorption spectra [1]. The resistivity can also be strongly influenced by impurities [2].

The nonmonotonous and complicated dependences of physical properties of dilute solutions with d-impurities were first explained by Friedel in 1956 [3], who has suggested the so-called virtual bound state (VBS) concept. By VBS we mean the mixture of d-state of the impurity atom and the conduction electron states. It is localized in a certain energy region and in the near vicinity of the impurity. The density of electron states has usually a Lorentzian form.

The thermal stability of the alloys in different non-equilibrium phases (amorphous, quasi-crystalline, metastable-crystalline), as well as in melts is one of the basic questions both for theoretical and practical reasons. Understanding the processes and the driving forces of the phase changes and the metastability of the actual states has a great importance in the improvemet of their mechanical properties and developing their other application, too.

Nowadays the effect of the electronic structure on the stability of the metallic systems is largely established [4, 5]. In most of the cases the density of electronic states (DOS) at the

[1]) 117234 Moscow, Russia.
[2]) Muzeum krt. 6–8, H-1088 Budapest, Hungary.
[3]) 48, North Portland Str., Glasgow G1 1XN, Great Britain.

Fermi energy (E_F) is relevant to the evaluation of the electronic effects, [6, 7]. This thinking has been started by Hume-Rothery's pioneer works [8] which was continued by a large number of scientists. The majority of these indeas, following the reformulated Hume-Rothery's rule by Mott and Jones [9], was concentrated on the interaction of the Fermi surface (FS) with the Brillouin zone (BZ) {or more accurately the Jones zone (JZ)} boundary. A special stabilization effect has been introduced by the FS $\Leftrightarrow$ JZ interaction, [9, 10].

The effect of the location of E_F in DOS is satisfactorily discussed for the stability of amorphous metals, [4, 11, 7]; the crystalline phases are much less discussed in this respect. However, in the special cases of metastable metallic systems it is clear that the chemical character and the size of the metalloid atom in a metal matrix has an influence on the position of the E_F in DOS, and depends directly on the solution heat of the metalloid [11]. Furthermore the free enthalpy (ΔH) has a minimum in the case when E_F is situated at the minimum of the DOS. So we are expecting that the investigations of E_F in DOS are much informative on the stability and general characterization of the alloy. Indeed, the stability of glasses is strictly correlated with the heat of solution in crystalline phase. This is the reason why we have chosen in our present paper investigations on the dependence of the heat of solution on the E_F position in dilute binary Cu-based alloys, (V, Co, and Fe alloying elements). These alloying elements are considered as single impurities, assuming that in the dilute alloying cases the interaction between the applied elements is negligible.

2. Method of Calculation

There exist several methods to determine the DOS and other relevant electronic parameters, based on first principle calculations. We are using the method of linear augmented plane waves (LAPW) treated by Green functions (LAPW-GF). The method in the frame of the muffin-tin potentials has been developed by Zeller and Dederichs [13, 14].

We are starting from the spectral representation of the Green function:

$$G(\boldsymbol{r}, \boldsymbol{r}', E) = \Omega_0/(2\pi)^3 \sum_{\lambda} \int_{\mathrm{BZ}} \Psi_{\boldsymbol{k}\lambda}(\boldsymbol{r})\, \Psi_{\boldsymbol{k}\lambda}(\boldsymbol{r}')\, (E - E_{\boldsymbol{k}\lambda})^{-1}\, \mathrm{d}\boldsymbol{k}\,, \tag{1}$$

where Ω_0 is the volume of the Wigner-Seitz cell, $\boldsymbol{r}$ and $\boldsymbol{r}'$ are the coordinate vectors, E is the energy, λ the band index, $\boldsymbol{k}$ the Bloch vector. Integration is carried out in the Brillouin zone, $\Psi_{\boldsymbol{k}\lambda}(\boldsymbol{r})$ is the electron wave function in the crystal, corresponding to the energy eigenvalue $E_{\boldsymbol{k}\lambda}$. We present $G(\boldsymbol{r}, \boldsymbol{r}', E)$ in the form of a series expansion based on the solutions of the Schrödinger equation in the muffin-tin (MT)-sphere [15, 16]

$$\begin{aligned} G(\boldsymbol{r} + \boldsymbol{R}^n, \boldsymbol{r}' + \boldsymbol{R}^{n'}, E) = {} & -i\delta_{nn'}\varkappa \sum_{L} R_l^n(r_<, E)\, Y_L(\boldsymbol{r})\, H_l^n(r_>, E)\, Y_L(\boldsymbol{r}') \\ & + \sum_{L, L'} R_l^n(\boldsymbol{r}, E)\, Y_L(\boldsymbol{r})\, G_{LL'}^{nn'} R_{l'}^{n'}(\boldsymbol{r}', E)\, Y_{L'}(\boldsymbol{r}')\,, \end{aligned} \tag{2}$$

where $r_< = \min(\boldsymbol{r}, \boldsymbol{r}')$, $r_> = \max(\boldsymbol{r}, \boldsymbol{r}')$, $L = (l, m)$ are the orbital quantum numbers, R^n and $R^{n'}$ are the atomic positions, $\varkappa = \sqrt{E}$;

$$H_l^n(\boldsymbol{r}, E) = R_l^n(\boldsymbol{r}, E) + iN_l^n(\boldsymbol{r}, E)\,,$$

where $N_l^n(\boldsymbol{r}, E)$ is the irregular solution of the radial Schrödinger equation, $G_{LL'}^{nn'}(E)$ are the energy-dependent coefficients of the Green function.

The first term in (2) represents a Green function for the MT sphere in vacuum and the second one characterizes the effect of the crystalline structure.

On the boundary of the MT-sphere the solution $R_l^n(r, E)$ field to the solution of the Schrödinger equation for free space is given by

$$R_l^n(r, E) = \mathrm{J}_l(kr) - i\sqrt{E}\, t_l^n(E)\, \mathrm{h}_l(kr)\,, \qquad (3)$$

$$H_l^n(r, E) = \mathrm{h}_l(kr)\,,$$

where $\mathrm{J}_l(kr)$ is the spherical Bessel function, $t_l^n(E)$ is the scattering matrix of the n-th MT-sphere, $\mathrm{h}_l(kr)$ is the first order spherical Hankel function.

The Green function coefficients of a crystal with defects may be expressed by the coefficients of the Green function for the ideal crystal [17, 18]:

$$G_{LL'}^{nn'}(E) = G_{LL'}^{0nn'}(E) + \sum_{n''L''} G_{LL''}^{0nn'}(E)\, \Delta t_{l''}^{n''}(E)\, G_{L''L'}^{n''n'}(E)\,, \qquad (4)$$

where $\Delta t_l^{n''}$ are the changes of the scattering matrix.

If the perturbation is regarded as highly localized (in the following we discuss the adequacy of such a supposition) and if angular momenta $l \leqq 2$ are taken into account, (4) assumes the form of four scalar equations

$$G_{LL}^{nn}(E) = G_{LL}^{onn}(E)\,[1 - G_{LL}^{onn}(E)\, \Delta t_l^n(E)]^{-1}\,. \qquad (5)$$

Therefore the basic problem is to determine the coefficients of the Green function for the ideal crystal, $G_{LL}^{onn}(E)$, $L = \{l, m\}$ set of quantum numbers.

We will start from the representation of the crystal wave functions in the LAPW method:

$$\Psi_{k\lambda}(r) = \sum_i a_i^{k\lambda} \varphi_{k_i}(r)\,,$$

$$\varphi_{k_i}(r) = \begin{cases} [\Omega_0]^{-1/2} \exp(ikr)\,; & |r| > R_s\,, \\ 4\pi R_s^2 [\Omega_0]^{-1/2} \exp(ik_i r_s) \sum i \Phi_L^s(k_i r)\, Y_L(r)\,; & |r| \leqq R_s\,, \end{cases} \qquad (6)$$

$$\Phi_l^s(k_i r) = a_{sl_i} R_{sl}(r, E_{sl}) + b_{sl_i} \dot{R}_{sl}(r, E_{sl})\,,$$

where the $a_i^{k\lambda}$ are the solutions of the secular equation in the LAPW method, $k_i = k + G_i$; G_i is a vector of the reciprocal lattice, R_s is the radius of the MT sphere for the s-th atom a_{sl_i} and b_{sl_i} are coefficient which can be determined from the condition of continuity of the wave functions on the boundary of the MT sphere; $R_{sl}(r, E_{sl})$ is the solution of the radial Schrödinger equation in the MT sphere, E_{sl} is the reference energy, $\dot{R}_{sl}(r, E_{sl})$ is its energy derivative.

Contrary to the case dealt with in the original KKR method, the $\Phi_L^s(k_i, r)$ depend implicitly on energy through the vector k. Direct substitution of $\Phi_L^s(k_i, r)$ into (2) is not possible.

Substituting (6) into (1) and multiplying (1) and (2) with the solution of the Schrödinger equation in the MT sphere and integrating we get

$$G_{LL'}^{nn'}(E)\, \alpha_l^{nn}(E)\, \alpha_{l'l'}^{n'n'}(E) = i\delta_{n'} \delta_{LL'} \varkappa \alpha_{ll}^{nn}(E)\, |\alpha_{ll}^{nn}(E)|$$

$$-2R_s^2 R \sum_{\lambda} \int_{\mathrm{BZ}} i^{l-l'} (E - E_{k\lambda})^{-1}\, \mathrm{d}k_i a_j^{k\lambda} (a_j^{k\lambda})^* \exp[i(k_i R^n - k_j R^n)]$$

$$+ \int_0^{R_s} \Phi_L^s(k_i, r)\, R_l^n(r, E)\, r^2\, \mathrm{d}r \int_0^{R_s'} \Phi_{L'}^{s'}(k_j r)\, R_{l'}^{n'}(r, E)\, r^2\, \mathrm{d}r\, Y_L^*(k_i)\, Y_{L'}(k_j)\,, \qquad (7)$$

where the $\alpha_{ll'}^{nn'}(E)$ coefficients are determined by the following formula:

$$\alpha_{ll'}^{nn'}(E) = \int_0^{R_s} R_l^n(r, E)\, R_{l'}^{n'}(r, E)\, r^2\, \mathrm{d}r\,. \tag{8}$$

Expanding $R_l^n(r, E)$ in powers of the energy and retaining only the constant and linear terms (following the method LAPW),

$$R_l^n(r, E) = [R_{sl}(r, E_{sl}) + (E - E_{sl})\, \dot{R}_{sl}(r, E_{sl})]\, [\alpha_{ll}^{nn'}(E)\, (1 + (E - E_{sl})^2\, N_{sl})^{-1}]^{-1/2}\,, \tag{9a}$$

where

$$N_{sl} = \int_0^{R_s} r^2\, \mathrm{d}r\, R_{sl}^2(r, E_{sl})\,. \tag{9b}$$

Finally we received

$$\begin{aligned}
&\mathrm{Im}\, [G_{LL'}^{nn'}(E)\, \big/ \sqrt{\alpha_{ll}^{nn}(E)\, \alpha_{l'l'}^{n'n'}(E)}] \\
&= \delta_{nn'}\delta_{LL'}\varkappa\, |\alpha_{ll}^{nn}(E)| - R_s^2 R_{s'}^2 \sum_{\lambda} \int_{\mathrm{BZ}} \delta(E - E_{k\lambda})\, \mathrm{d}k_i^{l-l'} \\
&\quad \times \sum_{ij} a^{k\lambda}(a^{k\lambda})^* \exp\, [i(\boldsymbol{k}_i \boldsymbol{R}^n - \boldsymbol{k}_j \boldsymbol{R}^{n'})]\, [a_{sl_i} + (E - E_{sl})\, b_{sl_i} N_{sl}] \\
&\quad \times [1 + (E - E_{sl})^2\, N_{sl}]^{-1/2}\, [a_{s'l'_j} + (E - E_{s'l'})\, b_{s'l'_j} N_{s'l'}] \\
&\quad \times [1 + (E - E_{s'l'})^2\, N_{s'l'}]^{-1/2}\, Y_L^*(\boldsymbol{k}_i)\, Y_{L'}^*(\boldsymbol{k}_j)\,.
\end{aligned} \tag{10}$$

The formula obtained has been applied to find the imaginary part of the Green function. The self-consistent potential of the matrix was determined by the LAPW-method. For the exchange correlation potential Vosko's parameterizing procedure [19] has been adopted.

Using the coefficients of the Green function defined in this way for crystals with defects it is easy to obtain the local density of states in the MT sphere

$$n(E) = -2\pi \int_{V_{\mathrm{MT}}} \mathrm{Im}\, G(r, r, E)\, \mathrm{d}r \tag{11}$$

and the electronic density

$$n(r) = -2\pi \int_{-\infty}^{E_{\mathrm{F}}} \mathrm{Im}\, G(r, r, E)\, \mathrm{d}E\,. \tag{12}$$

As a check of the imaginary part of the Green function so determined the density of states of (11) with the density of states got by the LAPW method and other methods has been compared. Modeling the ideal Cu crystal by regarding a Cu atom as an impurity in Cu, the deviation from the density of states of the ideal Cu crystal was small. A similar check was performed also for the local partial charge on Cu in the MT sphere. Local partial charges in the MT sphere for s-, p- and d-electrons are compared with LAPW values in Table 1, while the DOS of the pure Cu is given in Fig. 1.

The real part of the Green function is given by the Kramers-Kronig relationship

$$\mathrm{Re}\, G_{LL'}^{nn'}(E)\, \alpha_{ll'}^{nn'}(E) = \frac{1}{\pi} \int_{-\infty}^{+\infty} \mathrm{Im}\, G_{LL'}^{nn'}(E)\, \alpha_{ll'}^{ss'}(E)\, (E - E')^{-1}\, \mathrm{d}E\,. \tag{13}$$

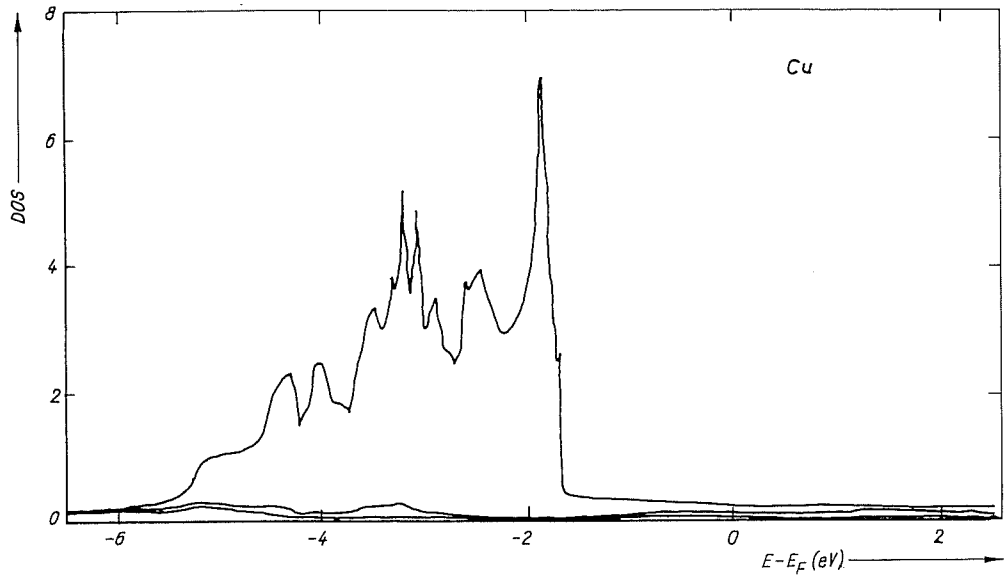

Fig. 1. Partial densities of electronic states of pure Cu metal. The curves from the bottom to the top are representing the states of s, s + p, and s + p + d, respectively

Equation (13) is calculated by quick Fourier transformation [20]. The upper limit of integration has been chosen as 2.5 Ry. The error so involved is negligible for the d-components of the Green function and for A_{1g} and T_{1g} components does not exceed 0.005 Ry^{-1}.

The error in our approach leads only to about 0.1 electron charge uncertainty in the MT sphere per electron density. Details of our computational procedure can be found in our earlier paper [21].

3. Results and Discussion

In the first stage the electronic structure of paramagnetic V, Cr, Mn, Fe, and Co point defects in the copper matrix was calculated. As an initial approximation we used the atomic electron density calculated by the Herman-Skilman method. The self-consistency was regarded as established if the integrated electron density did not change by more than 0.1%, between two successive iteration steps. Core states have been computed for each iteration step, i.e. in the calculation the relaxation effects of core states were included, too.

Table 1
Experimental energy position of maxima in VBS DOS in dilute alloy CuNi

method	$E_d - E_F$ (eV)
thermopower, [37] (N_d = 8.6 to 9.0)	-0.73 ± 0.01
photoemission [38]	-0.95
X-ray photoemission [39]	-0.8 ± 0.1
absorption [40]	-0.78

Table 2
Magnetic moment of impurities in Cu (in units of μ_B)

impurity	V	Cr	Mn	Fe	Co
calc. [41]	2.45	3.66	3.68	2.76	1.62
experimental					
[42]	0 (?)	2.46	3.96	–	–
[43]	–	3.9 ± 0.5	–	–	–
[44]	–	–	–	3.68 ± 0.17	–
[45]	–	–	4.93 ± 0.25	–	–
[46]	–	–	–	3.4	–
[47]	–	–	–	3.54	–
[48]	–	–	–	3.0 ± 0.4	–

In this sense the fulfillment of Friedel's sum rules up to an accuracy of 0.1 to 0.3 electrons can be regarded as a reasonably good result.

Our previous calculations [21] have established a relatively small magnetic moment for V, Mn, Cr, Co, and Fe imurities in Cu, which are summarized in Table 2. It is clear that the experimental values of the magnetic moments are of controversial nature. There are results finding no magnetic moment of V in Cu, but, on the other hand, experimental publications described a remarkable residual resistivity (18.4 μΩ cm/at% [22]) suggesting a considerable Kondo effect connected with the magnetic moment of V. Note, there is another

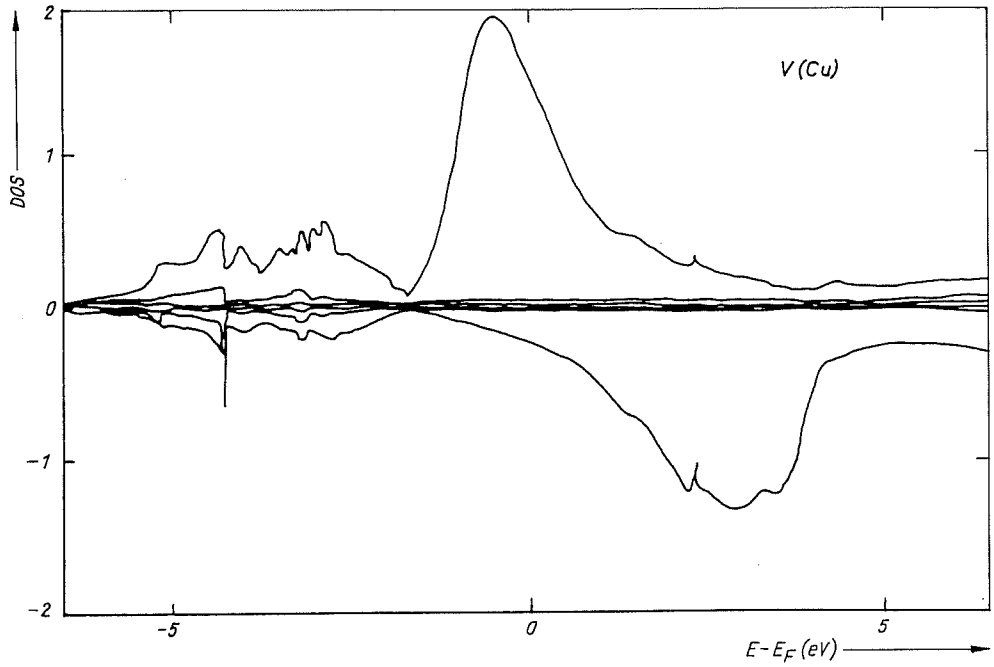

Fig. 2. Partial densities of electronic states of V impurity in Cu metal. Here and in the following figures the curves from the bottom to the top are representing the states of s, s + p, and s + p + d, respectively

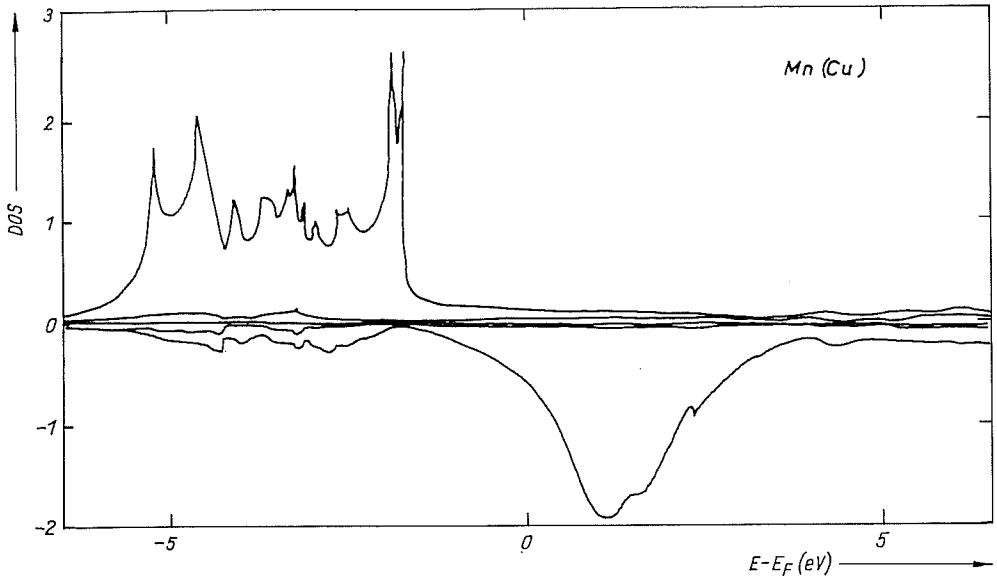

Fig. 3. Partial density of electronic states of Mn impurity in Cu

assumption [23]: the existence of a magnetic moment on V (and Co) in Cu, but it is proven [24, 25] that only a coupled pair of the Co impurity has a local magnetic moment [26], the single impurity has not. The work of [27], however, shows that the individual Co impurity has a magnetic moment, too, but only with a strong interaction with its nearest neighbors. For Fe impurity the experimental magnetic moments are (3.0 ± 0.4), 3.54, 3.4, and (3.68 ± 0.17) μ_B, [28 to 31].

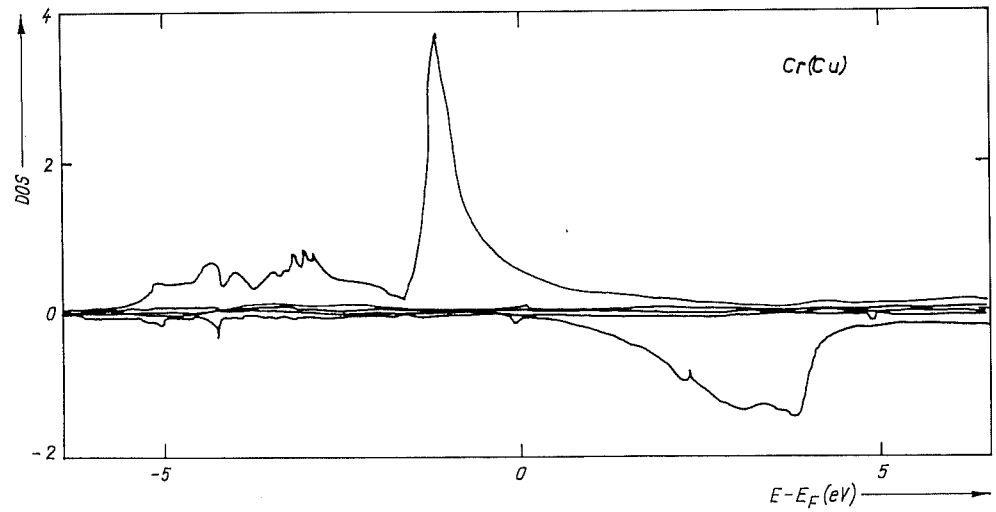

Fig. 4. Partial density of electronic states of Cr impurity in Cu

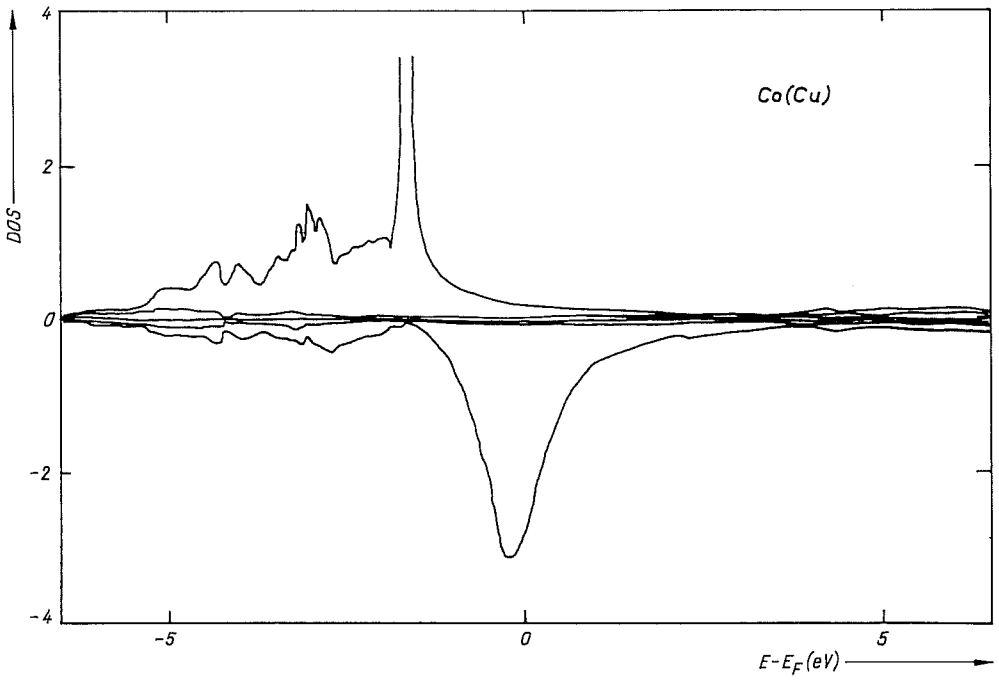

Fig. 5. Partial density of electronic states of Co impurity in Cu

Let us concentrate now on the calculated DOS curves, which are displayed on Fig. 2 to 6, for V, Mn, Cr, Co, and Fe, respectively. It is seen that the VBS for V, Fe, and Co appears in the vicinity of E_F, but for Mn and Cr the VBS peak is relatively far away from the Fermi level. Due to the peak at E_F, the systems create an additional energy which can be liberated at vanishing of this bond either by unifying with the conduction band either disappearing in the energy range over the E_F, this additional energy, however, not appears when there is no peak at E_F. In practice dilute V, Fe, and Co alloys with Cu show an instability [32]. For example in the equilibrium state of V in Cu when the concentration of V is higher as 7%, a segregation has been stated [33]. The concentrated CuCo alloy is not stable as well, forming a cluster of Co atoms in the matrix, [34], and the solubility of Fe in Cu is also very small. In this point of view the solubility of Mn in Cu is high enough, which can be expected from the DOS, where the VBS peak is situated well above the Fermi level. Cr is peculiar in this behaviour because its VBS is not so emphasized as for others, but lies well above E_F, too. In this case E_F is located on the tail of the DOS, having no stable minimum condition.

We can be sure that we are in the impurity approximation for the solubility, because the impurity–impurity interaction characterizing the system at higher concentrations will not promote further solubility but just the opposite. Consequently the highest solubility has to be expected in the extreme dilute case, as in our approximation.

In the experiment, such as photoemission and optical absorption, it was shown that the VBS is not present in dilute alloys of Mn, Fe, and Co with Cu [1, 30, 35, 36]. In theoretical calculations the VBS could be clearly displayed. The important result of this work is that

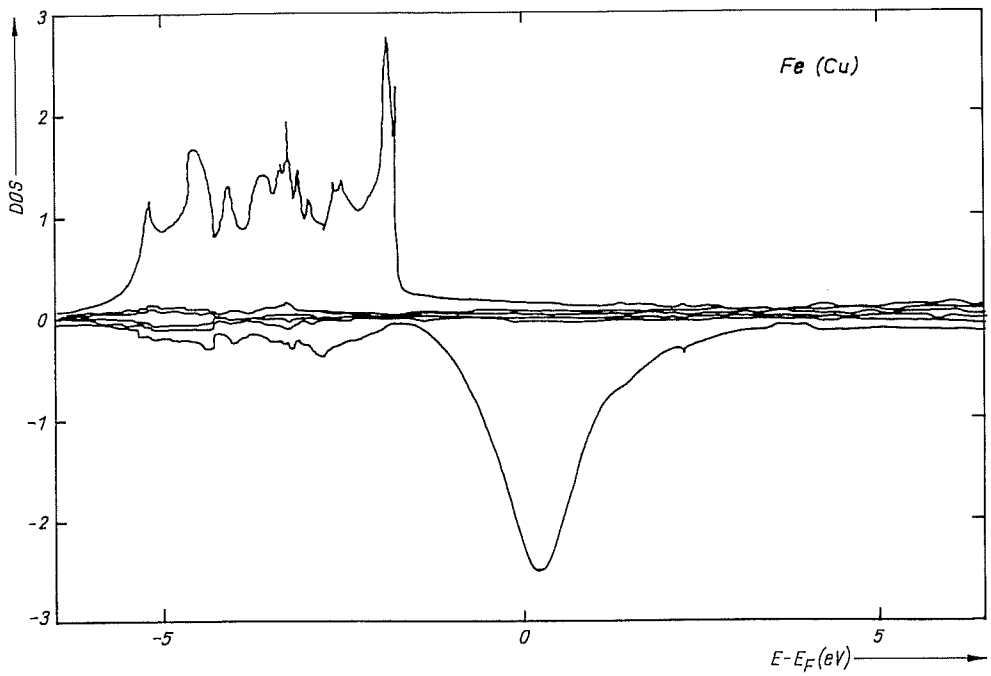

Fig. 6. Partial density of electronic states of Fe impurity in Cu

we unveiled the fact that VBS is strongly hybridized with d-states and is not revealed by optical measurements.

In conclusion we summarize this paper: we have calculated a strict correlation between the electronic density of states and solubility of 3d metals in Cu matrix.

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