Structural features and superconductivity of Al-doped Y(RE)-123-type single crystals

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Abstract. The structure of a series of highly Al-doped superconducting Y(RE)-123 (RE = rare earth element) single crystals was investigated by XRD and NMR methods. On the basis of the data obtained by the structural investigations combined with the studies of magnetic and optical properties, the formation of various superstructures in the samples of pseudo-tetragonal symmetry has been discussed. The correlation between the carrier concentration and T_c-values has been determined. The superconductivity (at 70 K) was indicated even at the 2/3 and 1/3 Al substitution for Cu in the basal and CuO_2 planes, respectively, in the phase presumably of a perovskite-like structural type.

1. Introduction

It is widely accepted that (i) the Y-123-type compounds of tetragonal symmetry are non-superconducting (NSC) and (ii) the superconductivity of the Y-123-type compounds of orthorhombic symmetry is suppressed by Al atoms which substitute for Cu in the basal plane and hence break the chains of the Cu–O squares. These statements have been justified by numerous experimental studies (see, e.g., [1–11]). However, a careful analysis has shown that the relationship between the structure and physical properties of the Al-doped Y(RE)-123-type compounds is more complicated and influenced by several factors.

In fact, only the $YBa_2Cu_3O_6$-type compound can be considered as a sample of tetragonal symmetry. At an increase of the oxygen concentration, an average tetragonal symmetry is realized only for a random distribution of anions in the basal plane. However, the presence of oxygen atoms in the basal plane is assumed to favour the formation of orthorhombic clusters. When Al atoms occupy the Cu1 sites, the oxygen atoms should present in the basal plane because the twofold coordination typical of Cu in the Cu1 site of the $YBa_2Cu_3O_6$-type structure is not suitable for trivalent Al ions. In addition, due to the octahedral coordination of Al by oxygen, the chains of Cu–O squares can be turned by 90° at the Al sites leading to the formation of a superstructure [12].

In the present work the structure of Al-doped Y(RE)-123 single crystals was studied in a series of samples of various Al contents. The structural features were investigated directly

by the XRD and NMR methods. The superconducting (SC) properties, which have been estimated by the measurements of magnetic susceptibility, were correlated to the particular structure of the single crystals under consideration and compared with the features in the corresponding optical spectra.

2. Experiment

Single crystals of the Y(RE)-123 type have been grown by a self-flux method in alumina crucibles. The initial load containing Y(RE) oxide, $BaCO_3$ and CuO in the ratio 3:25:72 was heated up to 1050–1100 °C and cooled down to the room temperature at a rate of 2–5 °C h^{-1}. Al atoms were present in the melt due to the interaction between the solution and crucible. The single crystals were separated by breaking apart the crucible. The chemical composition of the grown crystals was determined with an accuracy better than 3% by EPMA using a CAMECA analyser. The chemical composition data presented in table 1 are the values averaged over three to five samples obtained from the same crucible, each of them investigated at three to five points on the natural mirror-like surfaces. The chemical composition of the samples was confirmed by the structural refinement.

All the investigations were performed on as-grown single crystals. Based on the data obtained by the x-ray phase analysis and EPMA, the samples with particular features were selected from various growth runs. The lattice parameter a of the single crystals selected (table 1) was similar to that

Table 1. The characteristics of the investigated Al-doped Y(RE)-123 type samples determined from the single crystal refinement of the structure in the space group $P4/mmm$.

Sample No	1001	746	804	920	785	1106
Chemical composition	$Sm(Ba_{1.8}Sm_{0.2})$ $(Cu_{2.63}Al_{0.37})$ $O_{6.94}$	$GdBa_2$ $(Cu_{2.70}Al_{0.30})$ $O_{6.88}$	$Dy(Ba_{1.92}Dy_{0.08})$ $Cu_{2.80}Al_{0.20}O_{6.49}$	$Gd(Ba_{1.98}Na_{0.02})$ $(Cu_{2.68}Al_{0.17}Na_{0.15})$ $O_{6.55}$	$Sm(Ba_{1.86}Sm_{0.14})$ $(Cu_{2.64}Al_{0.36})$ $O_{7.1}$	$(Y_{0.57}Ca_{0.43})$ $(Ba_{1.56}Ca_{0.44})$ $(Cu_{1.73}Al_{1.27})O_{7.95}$
a (Å)	3.897(1)	3.894(1)	3.877(1)	3.887(1)	3.900(1)	3.873(1)
c (Å)	11.580(2)	11.702(3)	11.754(2)	11.660(3)	11.638(3)	11.767(2)
Rec. refl.	1124	1138	1147	1269	1245	1011
Uniq. refl.	242	226	236	246	248	197
Obs. refl. with $I > 2\sigma$	220	204	219	233	229	195
Final R obs. refl.	0.039	0.023	0.037	0.042	0.037	0.047
Site Cu1 (1a) (0 0 0)	0.63 Cu+ +0.37 Al	0.70 Cu+ +0.30 Al	0.80 Cu+ +0.20 Al	0.68 Cu+ +0.17 Al + 0.15 Na	Cu+ +0.36 Al	0.35Cu+ +0.65 Al
Site Cu2 (2g) (0 0 1)	2.00 Cu	2.00 Cu	2.00 Cu	2.00 Cu	2.00 Cu	1.38Cu+ +0.62 Al
Site O (2f) (0 1/2 0)	0.94 O	0.88 O	0.49 O	0.55 O	1.10 O	2.00 O
Site O (2g) (0 0 1)	2.00 O	2.00 O	2.00 O	2.00 O	2.00 O	1.95 O
Site O (4i) (1/2 0 l)	4.00 O	4.00 O	4.00 O	4.00 O	4.00 O	4.00 O

for tetragonal Y(RE)-123-type compounds. In contrast, the lattice parameter c of the selected samples was significantly lower than that for the samples of tetragonal (11.8 Å) and even orthorhombic (11.7 Å) symmetry [13]. The reduced c-values indicated a possible formation of a superstructure in the samples selected.

The x-ray data for six selected samples (table 1) were collected on a Philips PW1100 diffractometer. The preliminary space group symmetry and cell parameters were obtained from the $(\nu, \chi, \varphi)_{hkl}$ values of 37–48 reflections accurately well centred on the diffractometer with a program [14] which repeatedly improves the angular values corresponding the peak until the angles move by not more than $0.01°$. The data for all the compounds were analysed in the tetragonal space group $P4/mmm$. The intensities were measured at room temperature with a modified version of the Lehman and Larsen procedure [15] using Mo Kα radiation ($\lambda = 0.710\,69$ Å) and with a scan speed range of 2–16° min^{-1}. A check reflection, monitored every 100, did not alter significantly for all the six data collection times. The intensities were corrected for Lorentz and polarization effects and for absorption using the PSI scan method.

The first structure was solved with SIR97 [16] while for the remaining ones the coordinates obtained in the first refinement were employed. All the structures were refined with the SHELX93 [17] program. For all the structures the possibility of a further insertion of different atoms in sites different from those expected were checked.

Magic angle spinning nuclear magnetic resonance (MAS NMR) spectra were obtained using a Doty magic angle spinning probe with a Bruker AMX-500 multinuclear Fourier transform spectrometer. The samples were spun at approximately 6 kHz at an angle of 54.7° to the magnetic field. ^{27}Al MAS NMR spectra were recorded at a frequencies of 130.3 MHz with a spectral width of 125 kHz, 4 μm pulses and 0.1 s delay between pulses. Between 13 000 and 20 000 transients were recorded for each spectrum. Peak positions

were measured with reference to octahedral ^{27}Al in an aqueous solution of aluminium chloride.

The temperature dependence of the magnetic susceptibility was measured using a SQUID magnetometer MPMS-5, Quantum Design.

The optical spectra in the range 0.5–5.0 eV were obtained by a spectroscopic ellipsometry method. The measurement results were analysed in a two-media air-isotropic sample approximation and the pseudodielectric function was determined. This approximation was good enough to reveal particular optical features in the series of related samples.

3. Results

3.1. Structural studies

As follows from table 1, the structure of all compounds was successfully described by a tetragonal model with low values of the R-factor. The chemical composition obtained by the structural determination was in agreement with the results of EPMA performed on the other samples from the same crucible, indicating a good quality and compositional stability of the single crystals in each experimental run. It should be noted that the location of Na atoms on the Cu sites in the sample N 920 was justified also by our previous studies [18] according to which a substitution of Na for Y leads to an increase of the c-parameter value.

The ^{27}Al MAS NMR spectroscopy has revealed particular features of the environment for Al atoms in Al-doped Y(RE)-123-type crystals. The experimental data (figure 1) have shown various Al coordinations for sample No 1001: the coordination polyhedra were both tetrahedra and octahedra. In figure 1 the peak at 75.2 ppm is due to ^{27}Al in tetrahedral coordination and the broad peak at 12 ppm to ^{27}Al in octahedral coordination. All of the other peaks in the spectrum of sample No 1001 are spinning sidebands of the tetrahedral peak.
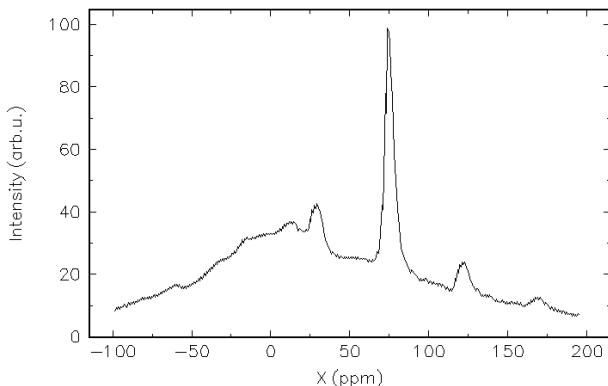
Figure 1. ^{27}Al MAS NMR spectrum of the sample No 1001.

3.2. Magnetic susceptibility measurements

Magnetic susceptibility measurements have shown the difference between the single crystals under consideration. Figure 2 presents the data for Al-doped Y(RE)-123-type samples along with the data for a standard SC Y-123-type single crystal of orthorhombic symmetry (No 1044, a = 3.827 Å, b = 3.899 Å, c = 11.711 Å, T_c = 92 K). The single crystals Nos 785 and 1001 (table 1) showed traces of an SC phase. The other Al-doped samples Nos 746, 804, 920 and 1106 were SC with the T_c-values equal to 50, 35, 40 and 70 K, respectively. However a direct correlation between the Al content on the one hand and T_c-values, shielding factor or lattice parameters on the other hand was not found.

The difference between the ZFC and FC shielding factors (figure 2) should be noticed. The difference is smallest for the sample No 804 in the series of Al-doped crystals under consideration. For this sample the transition region from the normal to the SC state is narrowest.

3.3. Optical data

As follows from the structural determination data (table 1), the oxygen concentration in the selected samples is different mainly due to a various occupation of the oxygen sites O(2f) in the basal plane. Therefore, the free carrier concentration should be different in these Al-based Y(RE)-123 compounds.

The analysis has shown that, with respect to the fine structure of the optical spectra, the samples can be divided into two groups. Typical optical spectra are presented in figure 3. The spectra of the samples Nos 1001 and 785 were characteristic for NSC samples [19]. A strong peak at 1.7 eV due to the charge-transfer optical transitions $d^9 \rightarrow d^{10}\bar{L}$ (where $\bar{L}$ is a hole in the p^6 shell of the O^{2-} ligands) in the CuO$_2$ plane is noticed. However, there is no optical feature in the region of 4.1 eV which is usually presented in the spectra of tetragonal compounds and is due to the $3d^{10} \rightarrow 3d^9 4p$ transitions of Cu$^+$ in the complex O(2g)–Cu1–O(2g).

The optical spectra of the other samples (Nos 746, 804, 920, 1106) indicate a higher carrier concentration which is revealed by a strong Drude-like contribution to the optical response (figure 3). As particular features of the sample No 1106, a complete suppression of the charge-transfer peak at 1.7 eV and a fine structure in the region 2–3 eV indicating possible changes in the CuO$_2$ plane are to be noted.
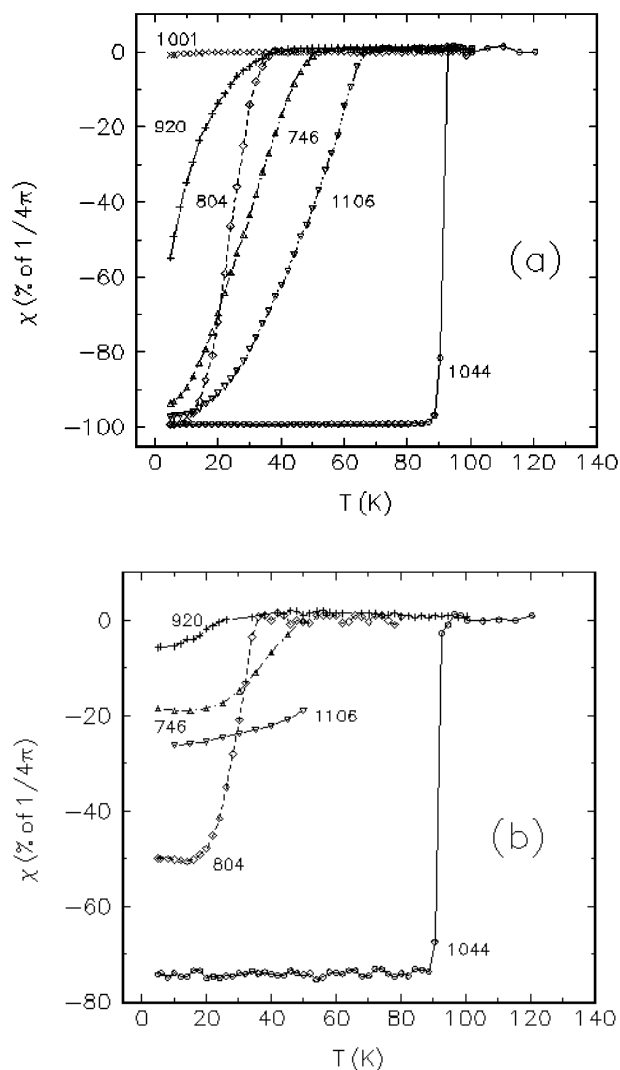

Figure 2. Zero-field-cooled (a) and field-cooled (b) magnetic susceptibility of the Al-doped Y(RE)-123-type SC single crystals. The data for a standard SC single crystal (No 1044) is shown for comparison. The curves are denoted by the sample numbers according to the data in table 1. Curves are guides for the eye.

The optical spectra of sample No 804 are similar to the typical spectra for SC Y-123-type compounds.

4. Discussion

The experimental data obtained show that the Al-doped crystals differ significantly from the standard Y(RE)-123-type samples. Therefore, it is reasonable to assume that particular features of highly Al-doped samples under investigation are due to a possible formation of a superstructure instead of a random distribution of Al and oxygen atoms in the basal plane. The structural models discussed below will take into account (1) a different occupation of the structural positions in various samples, (2) the presence of Al in a tetrahedral coordination in sample No 1001, (3) a high probability of formation of chains composed by Al–O tetrahedra as in cuprate $(Y_{1-x}Ca_x)Sr_2Cu_2GaO_7$ [20] of a brownmillerite structural
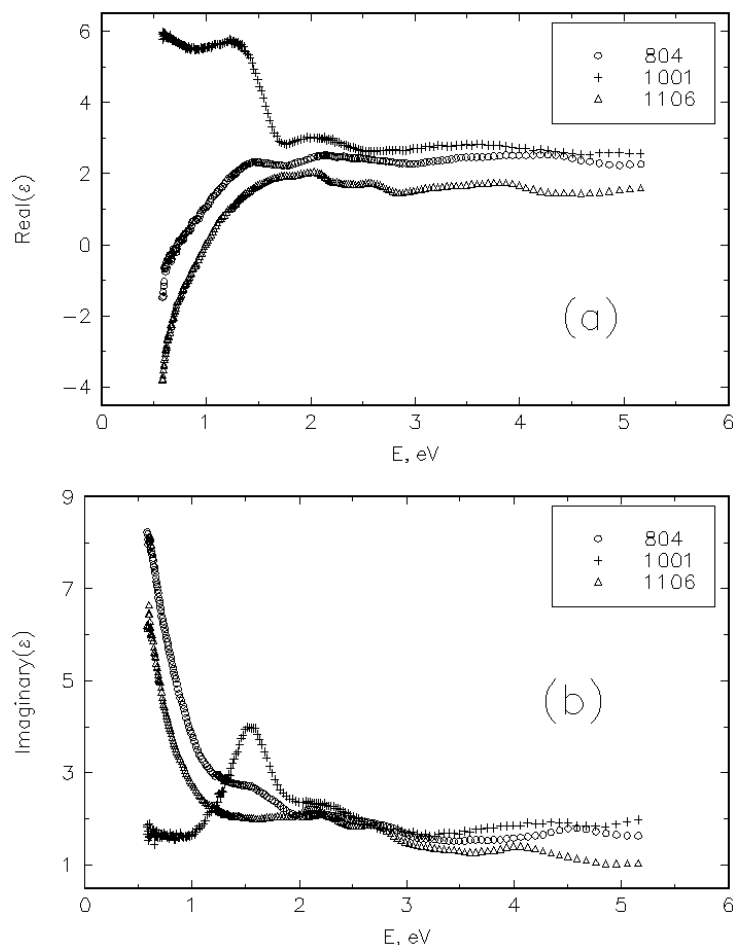
Figure 3. Real (a) and imaginary (b) parts of the dielectric function obtained from the ellipsometric measurements from the (*ab*)-plane of the samples Nos 1001 (crosses), 804 (circles) and 1106 (triangles).

type and (4) a small concentration of monovalent Cu ions in the basal plane of the investigated crystals.

Recently, the superstructure ($a_s = b_s = 3a\sqrt{2} = 15.5$ Å, $c = 23.3$ Å) was indicated in Al-doped Eu-123-type crystal [21], in which RE and Al amount was close to these in the sample No 1001. The superstructure (figure 4(a)) was similar to the model of a tetragonal lattice ($a_s = b_s = 2a\sqrt{2}$) for $YBa_2Cu_3O_{6+x}$ with the oxygen concentration $x = 7/8$ [22]. The model proposed for the sample No 1001 (figure 4(b)) represents the pseudo-tetragonal supercell with the Al and oxygen amount corresponding to these determined by XRD. According to the NMR data, Al is mainly in the fourfold coordination.

Having in mind the oxygen concentration ($x = 6.49$), the sample No 804 was assumed to possess structure similar to the ortho-II phase. The value of the *c*-parameter ($c = 11.754(2)$ Å) corresponds to that for a orthorhombic phase [13] taking into account that Y atoms were replaced by larger Gd atoms. Due to the presence of a high Al amount, the ortho-II structure should be distorted but the superconductivity was still observed. The substitution of Al for Cu1 resulted in a decrease of the T_c-value from 65 K typical for the ortho-II phase to 35 K.

The Al amount as well as the oxygen concentration in the basal plane is higher in the sample No 746 than in

No 804. This fact does not contradict the different shielding factor values in these samples (figure 2). A decrease of a *c*-parameter in No 746 as compared with No 804 can be probably caused by a higher Al amount.

The low values of the shielding factor in sample No 920 is possibly due to the presence of Na atoms in the basal plane. The formation of a superstructure along the *c*-axis due to the ordered distribution of Al and Na cations in the alternating layers can be proposed. In spite of the substitution of Cu by large Na atoms, this is a possible reason for a decrease of the *c*-parameter in sample No 920 as compared to No 746.

In the structural model proposed for sample No 785 (figure 4(c)) the Al ions were assumed to be in octahedral coordination. According to the model, the Cu ions in the basal plane are bivalent and the chains of the Cu–O squares are broken by Al-ions. However, in real crystals longer Cu–O chains can be formed, resulting in a trace of superconducting phase.

The structure of the sample No 1106 differs significantly from the other investigated structures. Though the lattice parameters are close to the Y-123 type, the cations are redistributed over various structural positions. The radii of cations in the Y and Ba sites become close, and the difference between CuO_2 and the basal plane reduces. The oxygen sites O(2fg) in the basal plane (figure 4(d)) are occupied
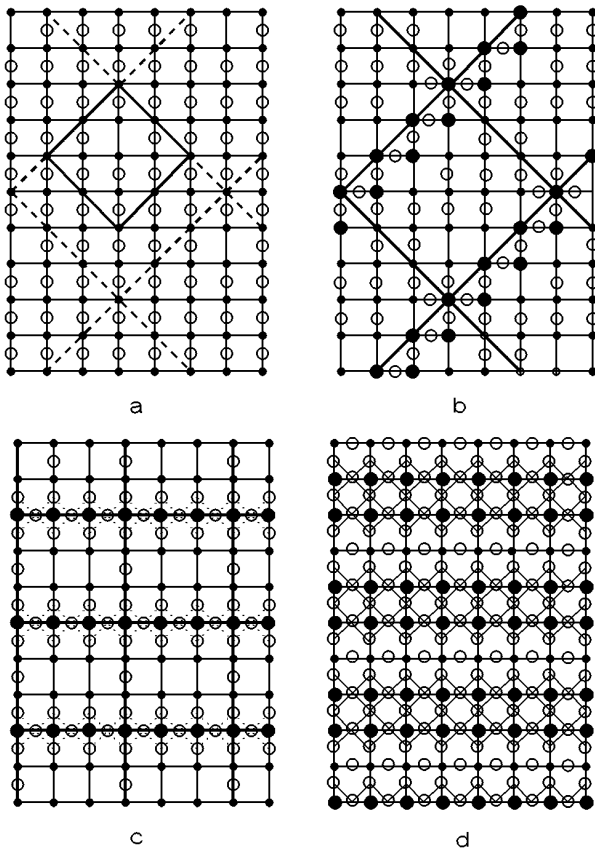
Table 2. Calculated hole concentration values $p(CuO_2)$, the energy of plasma maximum E_p and T_c-values for various Al-doped Y(RE)-123-type samples.

Sample No	$p(CuO_2)$	E_p (eV)	T_c (K)
1001	≈ 0	—	[a]
785	≈ 0	—	[a]
920	0.05	0.98	40
804	0.09	1.10	35
746	0.15	1.02	50
1106	0.17	1.12	70

[a] Trace of superconductivity.

Figure 4. The structural models for the basal plane of the Al-doped samples for YBa$_2$Cu$_3$O$_{6+x}$ with the oxygen concentration $x = 7/8$ [22] (a), No 1001 (b), Nos 785 (c), No 1106 (d). Small and large full and hollow circles are Cu, Al and oxygen atoms, respectively.

where R_0 and B are constants whose values have been tabulated for many bond types [25]. We set $B = 0.37$ as the best choice for most bonds [25]. The values of R_0 we take from [25] and [26]. The positive sign in (1) is taken for a cation and the negative one for an anion. The net hole concentration $p(CuO_2)$ in the CuO$_2$ planes can be calculated by summing the excess positive charge above +2 for Cu and -2 for O:

$$p(CuO_2) = V_{Cu} + 2V_O + 2. \qquad (2)$$

In the calculations the values of R_{ij} and the occupancy numbers have been calculated from the positions of the atoms determined by XRD. The results of calculations are given in table 2. It should be noted that the $p(CuO_2)$-values correlate with the plasma energy E_p which has been determined from the optical data and is directly related to the free carrier concentration. As can be seen, the critical temperature T_c increases with increasing concentration of the holes transferred to the CuO$_2$ plane. The relative changes in T_c against $p(CuO_2)$ are of similar magnitude as for other Y-123-type cuprates [24].

Summarizing, it should be noted that the analysis of the obtained experimental results has shown that superconductivity of highly Al-doped Y(RE)-123-type crystals can be related to the formation of a superstructure in the basal plane. Based on the assumption made in the present work, a series of new structural XRD studies on the same samples has been recently performed in order to indicate the presence of the superstructure. In the preliminary investigations the superstructural reflections for samples No 1001 and 920 have been revealed confirming hence the model for the structure of the Al-doped Y(RE)-123-type crystals developed in the present work. New structural data will be published elsewhere [27].

completely, leading to the octahedral coordination of cations in the Cu1 sites. The structure becomes intermediate between the infinite layer and perovskite type. The predicted transformation of the crystal lattice in Al-doped RE-123-type compounds into the perovskite-like structure is in agreement with the general regularities in the class of cuprates.

It should be noted that in the real crystals the superstructure illustrated by figure 4 is assumed to be distorted leading to a pseudo-tetragonal symmetry. The presence of Al atoms in octahedral coordination favours the rotation of the chains by 90°.

In order to estimate the effect of Al doping and structural features on the critical temperature T_c, it is useful to calculate the bond valence sums (BVSs) [23]. Although this method is rather semi-empirical, it can nevertheless help us to understand important trends when series of samples with various chemical compositions are compared (see also [24] for discussions and related references).

By definition, the sum of the bond valences around an ion gives its average valence. The bond valence sum, V_i, for ion i is calculated from the experimental bond lengths, R_{ij}, using the empirical relation:

$$V_i = \pm \sum_j \exp\{(R_0 - R_{ij})/B\} \qquad (1)$$

Acknowledgments

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