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## Classification

Physics Abstracts

74.10 — 74.70 — 63.20D

**Back to the A15 instability problems**A. F. Khoder (\*<sup>+</sup>), J. Labbé (\*\*), M. Couach (\*) and J. P. Sénateur (\*\*\*)

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**Résumé.** — De récents résultats expérimentaux sur les composés A15 permettent une meilleure compréhension de la relation entre la supraconductivité et l'instabilité de réseau dans ce système. L'effet de la déformation structurale est de réduire la température de transition supraconductrice  $T_c$ . Une augmentation de  $T_c$ , dans le cas de  $V_3Si$ , est obtenue lorsque la température de la transition structurale est abaissée (par effet de pression ou de défauts). Il est possible, d'un point de vue théorique, de comprendre et de prévoir ces effets dans le cadre des *modèles* Jahn-Teller de bandes, ce qui donne des arguments supplémentaires en faveur de ce mécanisme.

**Abstract.** — Recent experimental results obtained on A15 compounds allow a better understanding of the correlation between superconductivity and lattice instability in this system. The effect of the lattice distortion is shown to reduce the superconducting transition  $T_c$ . An enhancement of  $T_c$  in the case of  $V_3Si$  is obtained when the temperature of the martensitic transition is lowered (by pressure or defects). Theoretically, these effects are well explained and predictable within the frame work of the band Jahn-Teller « models »; then also give more arguments in favour of these models.

**1. Introduction.**

The anomalous physical properties of the A15 compounds have been known for a long time to be correlated with the high superconducting transition temperatures found in this class of compounds. Lattice instabilities, such as phonon softening and structural transition, strong temperature dependence of the susceptibility and the Knight shift are exhibited by the compounds  $V_3Si$  and  $Nb_3Sn$  which are the most studied compounds of the A15 family [1]. Moreover, the resistivity « saturation » with increasing temperature exhibited by the A15 [2] seems to be a general behaviour encountered in most of the d and f-band compounds.

Early in the sixties and seventies, models with a degenerate peak in the density of states at the Fermi level were proposed [3-5] and succeeded in accounting for the anomalous physical properties.

The origin of the degenerate peak of the density of states is admitted to be due to the particular disposition of transition atoms (V or Nb) along three orthogonal sets of linear chains in the A15 structure,

whatever the coupling between them. As far as the lattice instabilities are concerned, the band Jahn-Teller mechanism is the underlying one in the different proposed models which, in fact, should be considered as different versions (different  $N(E)$  shapes) of the band Jahn-Teller model as the latter, to be applicable, needs exactly what these versions share in common :

- a. degeneracy at the Fermi level  $E_F$ ,
- b. high density of states  $N(E_F)$ .

The Peierls instabilities model of Gor'kov [5] has also degeneracy (electron-hole) at  $E_F$  and singular density of states and, analytically, cannot be differentiated from the other models as has been shown in detail [6]. Although these different versions (or models) are not based on strong microscopic arguments (the anisotropy is too weak to justify a one-dimensional approximation of the band structure), the location of  $E_F$  close to a singularity of the density of states is shown to be a fact experimentally well established. Actually, the temperature of the structural transition  $T_m$  and the sign of the tetragonal distortion  $\varepsilon$  are extremely sensitive to a small variation of the number of electrons in the band whatever the way of obtaining such a variation (pressure, irradiation with low level of defects, chemical substitution, etc.).

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The clearest evidence of this sensitivity is given in a recently published paper [7] on the effect of experimental substitution of Sn by Sb in  $\text{Nb}_3\text{Sn}$ . A low temperature phase diagram of  $\text{Nb}_3\text{Sn}_{1-x}\text{Sb}_x$  was obtained by means of X-rays and it was possible to deduce the main characteristics of this experimental results theoretically by using the Labbé-Friedel version of the Jahn-Teller band model [8].

In this paper we will give new arguments supporting the Jahn-Teller band model by studying the connection between superconductivity and tetragonality and introducing the modifications of the band structure due to the lattice distortion  $\varepsilon$  in the calculation of  $T_c$  of the tetragonal phase.

Before going on, we recall the limitations of the Jahn-Teller band model in the case of A15.

First, this model does not prejudice of the strength of the electron-phonon interaction which, if strong enough, can provide a localisation of some phonon modes. This was recently pointed out by Yu and Anderson [9] and seems to explain the behaviour of resistivity and susceptibility at high temperature.

Second, the fine structure of  $N(E)$  is washed out by a strong or even moderate level of disorder. Then, the model is no longer adequate to study the effect of strong disorder on the physical properties of the A15 and especially the superconductivity which, for disordered systems, is mainly limited by the increase of the Coulomb disorder renormalized  $\mu^*$  parameter, as stated and pointed out by Anderson *et al.* [10] for strong disorder. But, for weak disorder, as we will show further, the behaviour of  $T_c$  exhibits some particularities which are well accounted for by the Jahn-Teller band model.

## 2. Experimental evidence of the $T_c$ -structural transformation relationship.

Experimental investigations of the effect of the lattice transformation on  $T_c$  for A15 were mainly motivated by the theoretical ideas concerning the favourable role of soft phonons in high  $T_c$  superconductivity [11].

Such ideas cannot be easily confirmed from an experimental point of view. In fact,  $\text{V}_3\text{Si}$  and  $\text{Nb}_3\text{Sn}$ , and other A15 compounds which show lattice instabilities, undergo a structural transition at a temperature  $T_m$  higher than  $T_c$  ( $T_m \simeq 21$  K for  $\text{V}_3\text{Si}$  and  $T_m \simeq 45$  K for  $\text{Nb}_3\text{Sn}$ ) and thus the phonon softening is more or less reduced. The high temperature soft modes stiffen in the low temperature phase before the occurrence of the superconducting transition ( $T_c \simeq 17$  K for  $\text{V}_3\text{Si}$  and  $T_c \simeq 18$  K for  $\text{Nb}_3\text{Sn}$ ). A confusing situation arises from the extreme sensitivity of the lattice transformation to defects. It appeared earlier that the occurrence of the lattice transition is correlated with the defect concentration in the sample. In the case of  $\text{V}_3\text{Si}$ , only the samples with a residual resistivity ratio (RRR) higher than 20 undergo this transformation and it is usual, in the A15's literature, to classify the samples in transforming,

non-transforming and even potentially transforming samples.

The superconducting transition temperature  $T_c$  of some non-transforming  $\text{V}_3\text{Si}$  samples has been shown to be higher than the  $T_c$ 's of the transforming ones [12]. If this fact gives a strong indication of the incompatibility between the lattice and the superconducting transitions, it also points out the need for more experimental investigations to clarify the way by which a *good transforming* sample can move to the *non-transforming* state. Moreover, the problem of the inhomogeneity of samples which obscures the definition of a precise critical temperature and the extent of the structural transformation has to be carefully considered.

The literature exhibits an important  $T_c$  spread which cannot always be explained by the sample quality (e.g. homogeneity) or measurement techniques.

It is a fact that inhomogeneity can often arise in single crystals which behave as an assembly of macroscopic subgrains with small differences in the physical properties. Also in order to investigate the particular properties of each subgrain and to achieve a  $T_c$  spectroscopy of the studied crystal we carried out AC susceptibility measurements which allow the different  $T_c$  regions of the sample to be seen by recording the imaginary part ( $\chi''$ ) of the susceptibility as a function of temperature in the vicinity of the superconducting transition [13].

The  $\chi''$  peak is associated with the occurrence of bulk superconductivity at scales larger than the penetration depth  $\lambda$  [14]. The temperature corresponding to the  $\chi''$  peak is taken as  $T_c$  <sup>(1)</sup>.

By means of this technique, many  $\text{V}_3\text{Si}$  samples, single crystals as well polycrystalline samples, were studied.

In the case of  $\text{V}_3\text{Si}$ , a complicated structure of  $\chi''$  peaks on a narrow temperature scale was found especially with single crystals (Fig. 1). The mosaic nature of such single crystals can be studied carefully by  $\gamma$ -ray diffraction [6, 15] which clearly shows the existence of many diffraction peaks, each corresponding to a subgrain (Fig. 2). Their number can be correlated to the number of  $\chi''$  peaks.

By applying a d.c. magnetic field, we could associate a critical field curve to each  $\chi''$  peak, thus characterizing the different grains of the samples. This analysis, in the case of  $\text{V}_3\text{Si}$ , is essential to clarify the origin of misunderstood anomalies at  $T_c$  observed by other measurement techniques such as the specific heat double-superconducting transition in  $\text{V}_3\text{Si}$  reported by Dayan *et al.* [16].

Figure 3 gives the results obtained for many samples of  $\text{V}_3\text{Si}$ , by plotting  $T_c$  as a function of the critical field

<sup>(1)</sup> We may suggest the use of the  $\chi''$  peak as an unambiguous physical criterion of  $T_c$  determination to be adopted by physicists.

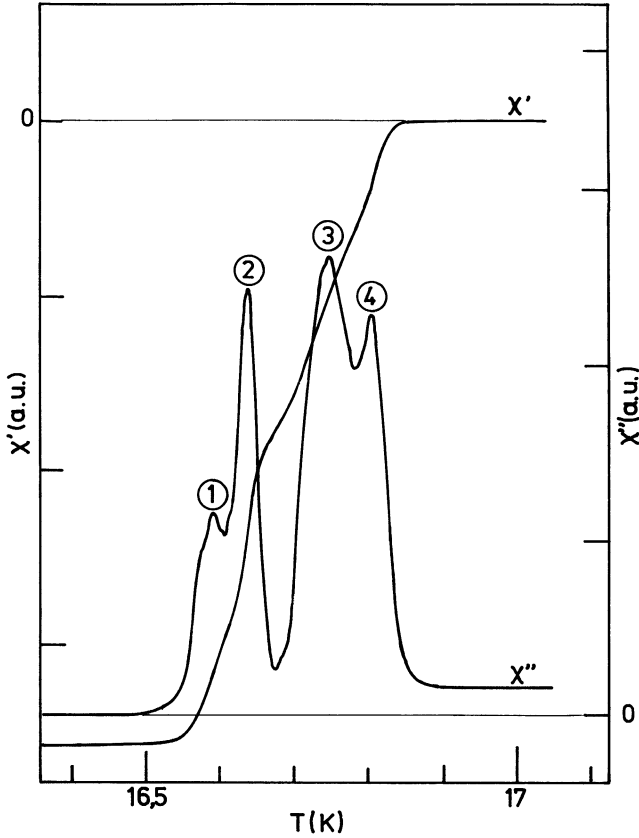


Fig. 1. — Result of an AC susceptibility measurement (frequency = 1 033 Hz, excitation field = 1 Oe, static field = 0) on a single crystal of  $V_3Si(S_5C_1)$  which shows at least four  $\chi''$  peaks. Peaks 1 and 2 correspond to the tetragonal phase, peaks 3 and 4 to the cubic phase, as shown by critical field slope measurements.

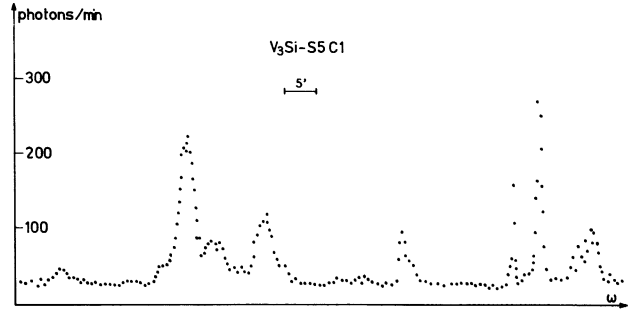


Fig. 2. —  $\gamma$ -ray diffraction rocking-curve at room temperature which reveals the mosaic nature of the same single crystal of  $V_3Si(S_5C_1)$  as shown in figure 1. Each peak corresponds to a subgrain. Only the narrowest peaks show a broadening for  $T < 20$  K indicating the occurrence of the tetragonality in the corresponding subgrains.

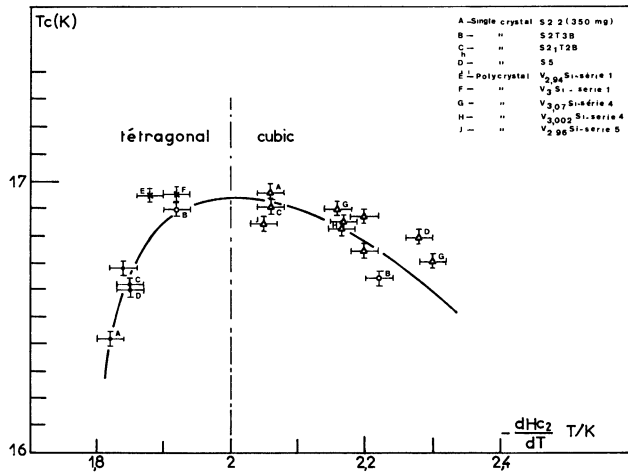


Fig. 3. — The relationship between  $T_c$  and  $-\frac{dH_{c2}}{dT}\Big|_{T_c}$  resulting from the study of different  $V_3Si$  samples, single crystals as well as polycrystals. Note that the same single crystal can contribute to both the tetragonal region and the cubic region.

slope  $-\frac{dH_{c2}}{dT}\Big|_{T_c}$ . This diagram clearly shows the effect of tetragonality on  $T_c$ .

The plot of  $T_c$  versus  $-\frac{dH_{c2}}{dT}\Big|_{T_c}$  displays a maximum which separates transforming (left side of the curve) from non-transforming  $V_3Si$  samples (right side of the curve). The main effect of the tetragonal distortion is a reduction of  $T_c$  and we estimate from figure 3 a reduction ( $\Delta T_c$ ) of 0.8 K for the purest  $V_3Si$  sample.

$\Delta T_c$  depends strongly on the value of the distortion  $\epsilon_c$  at  $T_c$ . This strong dependence  $\Delta T_c(\epsilon_c)$  is displayed by the increase of  $T_c$  with the increase of  $-\frac{dH_{c2}}{dT}\Big|_{T_c}$  within the tetragonal domain. In fact, the increase of the critical field slope is mainly due to an increase of the defect concentration which reduces  $T_m$  and thus the value  $\epsilon_c$  of the tetragonal distortion at  $T_c$ .

We should mention that this first increase of  $T_c$  with the defect concentration has been noticed by many authors studying the effect of irradiations on  $V_3Si$  [17]. A similar effect in  $Nb_3Sn$  and  $V_3Ga$  has also been pointed out by Karnezos and Weinstock

[18]. We studied this effect extensively [6] and similar results have been obtained recently by Khlopkin [19] although the height of the maximum of  $T_c$  is less important than that obtained in figure 2. An interesting result of Khlopkin [19] is the observation of the structural transformation at  $T_m$  below  $T_c$  when the superconducting transition is inhibited by a strong magnetic field.

### 3. The interaction between superconductivity and lattice transformation analysed by the Jahn-Teller band model.

The removal of the degeneracy of  $N(E_F)$  by the lattice distortion (Jahn-Teller band mechanism) and the new symmetry of the low temperature phase cause modifications of the Fermi surface shape.

The impact of the band structure modifications on  $T_c$  will depend on the strength of these modifications i.e. of the amplitude of the lattice distortion  $|\varepsilon_c|$  at  $T_c$ . Since the lattice distortion ( $\varepsilon$ ) increases as the temperature decreases, the value of  $|\varepsilon_c|$  will depend on the interval  $T_m - T_c$ . Changing this interval (by changing  $T_m$ ) will change  $|\varepsilon_c|$  and thus the effect of tetragonality on  $T_c$ .

Obviously, if the interval  $T_m - T_c$  is larger than  $T_m/2$ , as in the case of  $\text{Nb}_3\text{Sn}$ ,  $\varepsilon_c$  is quite temperature independent and we can anticipate that a few Kelvin change of  $T_m$  will have no effect on  $T_c$ .

Let us consider the Labbé-Friedel version of the Jahn-Teller band model of the A15 [4], where  $T_c$  is mainly related to,  $Q$ , the number of carriers in the peak of  $N(E)$ . For the cubic phase ( $\varepsilon = 0$ ) we have the two coupled equations [20] :

$$\begin{aligned} 2 k_B T_c &= B^2 V^2 L^2 \\ Q &= 12 B^2 V L K \end{aligned}$$

where  $B$  is a constant related to the shape of  $N(E)$  and  $V$  is the electron-phonon interaction constant.

$L$  and  $K$  are given by :

$$\begin{aligned} L &= \int_0^\infty \frac{\tanh(X^2 + \rho)}{X^2 + \rho} dx \\ K &= \int_0^\infty \frac{dx}{1 + \exp[2(X^2 + \rho)]} \end{aligned}$$

with

$$\rho = \frac{\xi_m}{2 k_B T_c}$$

$\xi_m$  being the interval between the Fermi level and the singularity (the bottom of the band). The relation  $T_c(Q)$  is obtained by eliminating  $\rho$ .

The corresponding set of equations for  $T_c^t$  of the distorted phase ( $\varepsilon \neq 0$ ) can be easily obtained [6] :

$$\begin{aligned} 2 k_B T_c^t &= B^2 V^2 (\alpha L_1 + (1 - \alpha) L_2)^2 \\ Q &= B \sqrt{2 k_B T_c^t} (\beta K_1 + (12 - \beta) K_2) \end{aligned}$$

where

$$\alpha = \frac{1}{3} \quad \text{and} \quad \beta = 4 \quad \text{for} \quad \varepsilon = \frac{c}{a} - 1 < 0$$

and

$$\alpha = \frac{2}{3} \quad \text{and} \quad \beta = 8 \quad \text{for} \quad \varepsilon = \frac{c}{a} - 1 > 0.$$

$L_1$  and  $K_1$  have the same expressions as  $L$  and  $K$ .  $L_2$  and  $K_2$  are given by the same integrals with  $\rho$  replaced by :

$$\rho_2 = \rho + \frac{3}{4} \frac{a \cdot q \cdot W}{2 k_b T_c^t} \cdot |\varepsilon|$$

where  $a$  is the distance between transition atoms on the chain,  $q$  the Slater coefficient which governs the expo-

ponential decrease of the d-orbital function and  $W$  is a band scale parameter.

In the derivation of the last equations for  $T_c^t$  and  $Q$ , we kept the same  $V$  as in the cubic phase. This assumption is justified by Anderson's Theorem [21] for low frequency phonons (seen as static defects) and supported by many recent theoretical papers which pointed out the negligible effect of the phonon softening on the enhancement of  $T_c$  [22].

Eliminating  $\rho$  now gives  $T_c^t$  as a function of  $|\varepsilon|$  for different  $Q$ . This result is drawn in figure 4 where the reduction of  $T_c$  is shown to be proportional to  $\varepsilon^2$  and quite negligible for high values of  $Q$  (i.e.  $E_F$  far from the peak of the density of states).

In the case of  $\text{V}_3\text{Si}$  and  $\text{Nb}_3\text{Sn}$  and with the parameters of the Labbé-Friedel model [4], the reduction of  $T_c$  is estimated to be 0.7 to 1.6 K ( $2.5 \times 10^{-3} < |\varepsilon| < 4 \times 10^{-3}$ ). This estimation scales with the experimental result of figure 3. Modifications of the density of states  $N(E_F)$  can be produced by different ways : disappearance of the fine structure of  $N(E_F)$  by introducing defects, partial or full removal of degeneracy by uniaxial stress, moving the Fermi level position by hydrostatic pressure or by a substitution element, etc. The parameter  $p$  which is used to modify the band structure will have a « direct » effect on  $T_m$ .  $T_c$  will be *directly* affected by the band structure modifications due to  $p$  and *indirectly* by the modification of  $T_m$  (i.e. of the distortion amplitude  $|\varepsilon|$  at  $T_c$ ). We will show that the indirect effect is by far the most important. If we accept for  $|\varepsilon|$  the expression given by a *mean field* phase transition theory :  $|\varepsilon| \sim \left(1 - \frac{T}{T_m}\right)^{1/2}$  for temperatures not far from  $T_m$  we will have

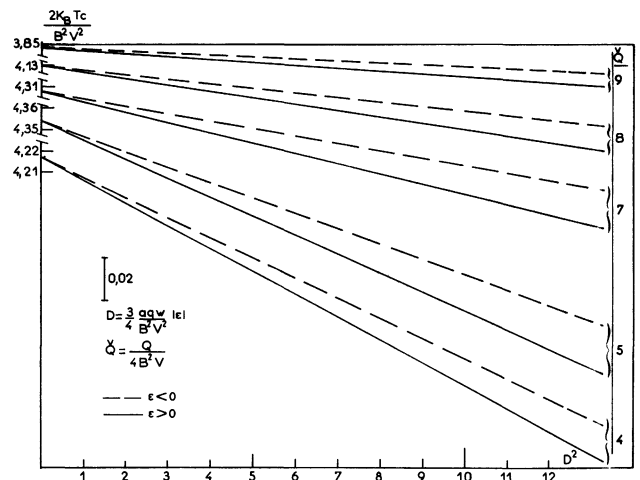


Fig. 4. — Effect of the tetragonality (distortion  $\varepsilon$ ) on the critical temperature  $T_c$ . This diagram shows that  $T_c$  behaves as  $\varepsilon^2$  and that this dependence smooths as the electron content of the d-band increases.

(as  $T_c^t - T_c \sim \varepsilon^2$ ) at  $T_c^t$

$$T_c^t - T_c = -a \left( 1 - \frac{T_c^t}{T_m} \right)$$

where  $a$  is a positive constant to be determined and  $T_c$  is the superconducting transition temperature of a virtual cubic phase.

The last expression is convenient in the case of  $V_3Si$  because  $T_c^t$  is close to  $T_m$  and the expression used for  $|\varepsilon|$  is still valid.

If we consider the known values of  $T_c$ ,  $T_m$  and the estimated value of the  $T_c$  reduction ( $\sim 1$  K) we find  $a \sim 5$  K.

The derivation of the last expression with respect to the parameter  $p$  gives :

$$\left( 1 - \frac{a}{T_m} \right) \frac{\partial T_c^t}{\partial p} = \frac{\partial T_c}{\partial p} - a \frac{T_c^t}{T_m^2} \frac{\partial T_m}{\partial p}.$$

As far as  $T_m$  is not strongly depressed, i.e. the Fermi surface is weakly perturbed by  $p$ , we can neglect  $\frac{\partial T_c}{\partial p}$  in the right side of the equation, because  $T_c$  is far less sensitive to the Fermi surface perturbation, as was shown by Labbé [4].

The « direct » term  $\frac{\partial T_c^t}{\partial p}$  becomes important in the case of strong modifications of the band structure : high pressure, high level of defects, etc.

The simplified equation

$$\left( 1 - \frac{a}{T_m} \right) \frac{\partial T_c^t}{\partial p} = -a \frac{T_c^t}{T_m^2} \frac{\partial T_m}{\partial p}$$

concerns the indirect effect of  $p$  on  $T_c^t$  due to the lattice distortion and shows an initial increase of  $T_c^t$  with the decrease of  $T_m$  before the direct term starts to interfere in a consequent way.

This equation explains the behaviour of  $T_c$  shown in figure 3 and the initial increase of  $T_c^t$  for small irradiation doses [17, 18].

Another related observation of this effect, in the case of  $V_3Si$ , is the dependence of  $T_c^t$  and  $T_m$  on hydrostatic

pressure studied by Chu and Testardi [23], who obtained

$$\frac{\partial T_c^t}{\partial p} / \frac{\partial T_m}{\partial p} = -0.24$$

while for this ratio the above equation yields the value of  $-0.27$ , surprisingly close to the experimental one.

Finally, the observed insensitivity of  $T_c$  to low fluences of neutron or  $\alpha$ -particle irradiation of  $V_3Si$ ,  $Nb_3Sn$  and other A15 [24] which suggest the existence of a *threshold fluence*, apart from the experimental uncertainties about the determination of  $T_c$  should be considered as another argument in favour of the above considerations. The observed insensitivity is only due to the competition between the *direct* effect of irradiation which tends to decrease  $T_c$  and the *indirect* effect, a consequence of the tetragonal distortion which, on the contrary, tends to increase  $T_c$ .

#### 4. Conclusion.

Although the microscopic origin of the singular density of states  $N(E)$  at the Fermi level is still controversial, many experimental results support the existence of a degenerate peak of  $N(E)$  as we pointed out above.

The observed incompatibility between superconductivity and lattice distortion in A15's as evidenced by the first increase of  $T_c$  with disorder in  $V_3Si$ , is well accounted for by the band Jahn-Teller model considered in this paper.

We should insist on the fact that such a model is no longer adequate for the strongly disordered A15. In this case, as shown by Anderson *et al.* [10], the decrease of  $T_c$  is governed by another physical mechanism based on the increase of the Coulomb parameter  $\mu^*$  with disorder.

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