Correlation between electronegativity and superconductivity

R. Asokamani and R. Manjula*
Department of Physics, College of Engineering, Anna University, Madras 600 025, India
(Received 6 September 1988)

This paper brings out one of the striking features exhibited by all oxide superconductors. It is found that irrespective of the value of T_c, the average electronegativity χ of all the oxide superconductors found up until now lies between 2.5 and 2.65 in the Pauling's scale and this is considered to be one of the criteria for oxide materials to be considered superconductors. This narrow range is in contrast to the elemental superconductors whose values lie in a broad range from 1.3 to 1.9. Further, the pressures required to drive some of the elemental metals to become superconductors have been calculated on the basis of their electronegativity values. The pressures so obtained agree well with the experimental observations and those calculated on the basis of band theory. The average electronegativity of $A15$ and Chevrel-phase superconductors are also given. Based on the concept of electronegativity the other oxide systems which are likely to become superconductors have been suggested.

I. INTRODUCTION

With the advent of high-T_c superconductors the quest for speculating a criterion for materials to have high transition temperature has increased. It is seen that by cascading more numbers of Cu-O layers T_c has increased in the recently discovered high-T_c compounds.[1] In this paper we put forward one of the criteria that should be satisfied by all oxide compounds to be superconductors. We have worked out the average electronegativity χ of a number of oxide superconductors and we observe that all of them have electronegativity values falling in a very narrow range of 2.5 to 2.65 whereas the electronegativity of elemental superconductors lies in a rather broad range varying from 1.3 to 1.9.[2] It is well known that a number of elements become superconductors by the application of high pressure.[3] This phenomenon of pressure-induced superconductors in metals such as Li, Y, Ba, and Lu has been successfully explained by us on the basis of band-structure calculation with McMillan's formula.[4-7]

Apart from metals, nonmetals such as Si, P, and S also become superconductors under pressure. Pressure-induced superconductivity in Si has been explained by us on the basis of band-structure results.[8] We now approach the same problem from the point of view of electronegativity. For elemental superconductors we can say that electronegativity values are centered around 1.6 ± 0.3. As far as elemental solids are concerned, the question that we raise is the following: What pressures are required to make Ba and S become superconductors? Ba and S have 0.93 and 2.2 as their respective electronegativity values. From the point of view of electronegativity the above question can be recast as follows: What pressure does Ba need to increase its χ value from 0.93 to approximately 1.6 and what pressure is to be applied for S to push down its χ value again in the vicinity of 1.6, from 2.2? The latter question carries more significance as it refers to the case of transformation of the nonmetal into metal and, hence, to a superconductor under pressure. This is analogous to La_2CuO_4 and $YBa_2CuO_{6.5}$. These are magnetic insulators which upon doping are made to become metallic and superconducting because of the increase in chemical pressure.

This paper is divided into three sections. Section A deals with the electronegativity of metals and the method of calculating the pressures required to drive the nonsuperconducting metals to become superconductors. In Sec. B, we discuss the average electronegativity of all oxide superconductors and the variation of the average χ value as a function of oxygen concentration in 1:2:3 systems. Section C is devoted to the discussion of average χ value possessed by all kinds of compounds of perovskite structures as well as some of the Chevrel-phase systems. Last, the unique range of χ values possessed by superconducting oxides leads us to suggest the possible compositions which will become superconductors either under application of external pressure or by increasing chemical pressure by making substitutions in the matrix. All the calculations that have been done here are based on the Pauling's scale. The electronegativity values of the elements used in this paper are taken from the recent work of Luo and Wang.[2]

II. AVERAGE ELECTRONEGATIVITIES

A. Electronegativity and superconductivity in elements

Pauling[9] introduced the concept of electronegativity by which he qualitatively described the transition from ionic to covalent bond. He observed that the electronegativity of metallic elements is less than 2 and that of nonmetallic elements greater than 2. This value of 2 in the electronegativity scale distinguishes metals from nonmetals. Luo and Wang[2] have made a detailed study of electronegativity of all elements and found that all superconducting elements are concentrated in a region where χ varies from 1.3 to 1.9. They observed that both very high and very low values of electronegativity do not favor superconductivity and all elemental superconductors have their electronegativity values falling in the above range. On this

basis, they defined this range as the criterion for superconductivity in elemental solids.

It is well known that metals such as Li, Y, Ba, and Lu do not exhibit superconductivity at ambient pressure and they start superconducting when they are subjected to high pressures. This phenomenon which we have explained on the basis of band structure calculations for the above-mentioned metals[4-8] is now being approached from the point of view of electronegativity. The elemental metals such as Ba, Li, Y, and Lu have their electronegativity values less than 1.3. For instance the value of χ for Ba is 0.93. In order to determine the pressure required to make the material become a superconductor, we calculate the pressure required to push the value of χ in the range 1.3–1.9, the range exhibited by elemental superconductors.

χ as a function of pressure has been calculated using Gordy's definition of electronegativity,[10] $\chi = Z_{\text{eff}} e/r$ where Z_{eff} is the unscreened nuclear charge and r is the covalent radius. The variation of r with pressure is found by proportionately decreasing the atomic radius from the known values of change in cell volume as a function of pressure. The changes in cell volumes adopted here have been already used in the band-structure calculations. It is interesting to observe that at 40 kbar, the χ value of Ba enters into the range 1.3–1.9. This is in good agreement with the experimental observation as well as our theoretical calculations based on band structure approach. Similar calculations that were done for the elements Y, Lu, and Li have been given in Table I. The calculated pressures for all the above metals at which χ goes above 1.3 are in good agreement with the experimental observations and the theoretical band-structure predictions.

TABLE I. Variation of χ with pressure.

Pressure (kbar)	V/V_0	$\chi = \frac{(Z_{\text{eff}})e}{r}$
Element: Ba		
0	1	0.930
10	0.908	1.024
20	0.865	1.075
30	0.788	1.180
40	0.744	1.315
50	0.707	1.345
Element: Y		
0	1	1.200
10	0.986	1.217
20	0.950	1.263
30	0.930	1.290
40	0.913	1.314
50	0.866	1.385
Element: Lu		
0	1	1.100
10	0.976	1.127
20	0.955	1.152
30	0.938	1.173
40	0.922	1.193
103	0.843	1.420
157	0.779	1.540
191	0.747	1.606
230	0.720	1.670
Element: Li		
0	1	0.960
247	0.520	1.850
Element: Sc		
0	1	1.300
170	0.765	1.690

B. Electronegativity of oxide superconductors

We have determined the average electronegativity of the different oxide superconductors starting with $Ba_{0.1}Sr_{0.9}TiO_3$ which has a T_c of 1 K to $Tl_2Ba_2Ca_2Cu_3O_{10}$ whose T_c is about 125 K. The striking feature that we observed was that the average electronegativity lies in a very narrow range, from 2.50 to 2.65. Even the newly found system which does not have copper in its composition, viz., $Ba_{0.6}K_{0.4}BiO_3$, which has a T_c of 30 K has a χ value of 2.63. The average χ values were calculated for as many as 40 different compositions of 1:2:3 system and it was found that for all of them χ is centered around 2.6. The most recently found high-T_c compounds (see Refs. 35 and 36 and their T_c values given in Table II) further strengthens our criterion. These values are given in Table II along with other systems.

According to Sanderson,[11] when two or more atoms initially different in electronegativity combine chemically they become adjusted to an equal intermediate electronegativity in the compound. Further, in the recent work of Villars and Phillips[12] on high-temperature superconductors, they combine two elements which are chemically closer and call it a pseudoelement and proceed to show that all superconductors with $T_c > 10$ K lie in three groups in their quantum structural diagrams. Here we calculate the average electronegativity χ of the system for various superconductors using the expression

$$\chi = \sum_{i=1}^{n} \chi_i N_i \Big/ \sum_{i=1}^{n} N_i ,$$

where N_i is the number of atoms of a particular species having electronegativity χ_i.

From the above studies, we propose that one of the criteria for oxide materials to be superconductors is that their average χ value should be in the range 2.5–2.65. But the converse is not true. This is borne out from the fact that the perovskite compound $La(Mg_{0.5}Nb_{0.5})O_3$ has a χ value of 2.63 and it is not superconducting.

C. Electronegativity of Chevrel phase and other systems

In Table II we have also listed the average χ values of conventional superconductors, Chevrel phase compounds, and those of nonsuperconducting oxides of perovskite structure. Figure 1 shows the plot of electronegativity

TABLE II. Electronegativity and transition temperature of various compositions.

Composition	T_c (K)	χ	Reference
Conventional nonoxide superconductors			
$LuRhB_4$	11.7	1.85	13
Mo_3Al_2C	10.0	1.77	14
Mo_2BC	7.0	1.97	15
$Sc_5Rh_4Si_{10}$	8.5	1.69	16
$Y_5Os_4Ge_{10}$	8.7	1.716	17
$YbRh_{1.4}Sn_{4.6}$	8.6	1.65	18
ZrRuP	13.0	1.83	19
NBPS	12.5	2.13	20
$LaRu_4P_{12}$	7.2	2.05	21
$Cu_{1.8}Mo_6S_6$	10.8	2.13	22
$Mo_6S_6I_2$	14.0	2.01	23
$Pb_{0.9}Mo_6S_{7.5}$	15.2	2.16	24
Antiferromagnetic superconductors			
$NdRh_4B_4$	5.36	1.87	25
$SmRh_4B_4$	2.72	1.87	25
Chevrel phase superconductors			
$NdMo_6S_8$	3.3	2.15	25
$ErMo_6Se_8$	6.0	1.77	25
Reentrant superconductors			
$ErRh_4B_4$	8.7	1.87	26
Ferromagnetic superconductors			
$Ho_{0.5}Eu_{0.5}Mo_6S_8$	2.0	2.14	27
Oxide superconductors			
NbO	~1.0	2.55	
TiO	~1.0	2.60	
$Ba_{0.1}Sr_{0.9}TiO_3$	1.0	2.63	28
$Li_{1.1}Ti_{1.9}O_4$	10–12	2.61	14
$Li_{1.2}Ti_{1.8}O_4$	10–12	2.60	14
$Li_{1.3}Ti_{1.7}O_4$	10–12	2.59	14
$BaPb_{0.8}Bi_{0.2}O_3$	13.2	2.61	29
$LiTi_2O_4$	13.7	2.62	30
$Ba_{0.6}K_{0.4}BiO_3$	30	2.63	31
$La_{1.8}Sr_{0.2}CuO_4$	40	2.64	32
$Tl_2Ba_2CuO_6$	83	2.53	1
$Bi_2Sr_2CaCu_3O_{10}$	85	2.64	33
$Bi_2Sr_2CaCu_2O_8$	90	2.57	33
$YBa_2Cu_3O_7$	90	2.58	34
$Tl_2Ba_2CaCu_2O_8$	118	2.52	33
$Tl_2Ba_2Ca_2Cu_3O_{10}$	125	2.50	33
$Pb_2Sr_2Y_{0.5}Ca_{0.5}Cu_3O_8$	68	2.51	35
$RBa_2Cu_4O_8$	57–81	2.60	36
Nonsuperconducting oxides (perovskite structure)			
$La(Co_{0.5}Ir_{0.5})O_3$	· · ·	2.72	28
$La(Mg_{0.5}Nb_{0.5})O_3$	· · ·	2.64	28
$La(Mn_{0.5}Ir_{0.5})O_3$	· · ·	2.81	28
$La(Mn_{0.5}Ru_{0.5})O_3$	· · ·	2.80	28
$La(Ni_{0.5}Ru_{0.5})O_3$	· · ·	2.74	28
$La(Ni_{0.5}Ti_{0.5})O_3$	· · ·	2.73	28
$LaTiO_3$	· · ·	2.70	28
$LaVO_3$	· · ·	2.70	28

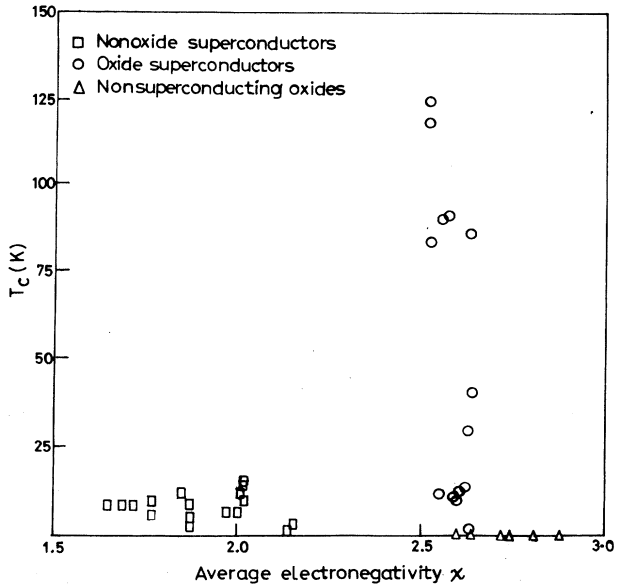

FIG. 1. Plot of average electronegativity vs transition temperature for nonoxide, oxide superconductors, and nonsuperconducting oxides of perovskite structure.

versus T_c of all materials and it is clearly seen that oxide superconductors cluster in a narrow region, irrespective of the value of T_c. We observe that the conventional nonoxides have χ values well below that of oxide systems, which we have discussed so far. Chevrel phase compounds as well as other compounds have low χ values. On the other hand, the nonsuperconducting oxides of perovskite structure are found to have χ values above those of the oxide superconductors, which are of present interest.

Encouraged by the results we have presented in Sec. A with regard to elemental substances, we speculate that materials like $LaTiO_3$, $LaVO_3$, and $La(Mg_{0.5}Nb_{0.5})O_3$, which have χ in the vicinity of the upper bound of the oxide systems, would become superconductors either by applying external pressure or by proper substitution by different atoms. Our expectation is in analogy with the nonmetal such as S which is made to become a superconductor under pressure where its χ value should be brought down below 1.9 from its actual value of 2.6.

Further, from the point of view of electronegativity, we suggest some of the oxide materials which are similar to $Tl_2Ba_2CaCu_2O_8$ as the probable candidates for superconductivity. Their average electronegativity values lie well

TABLE III. Compositions similar to $Tl_2Ba_2CaCu_2O_8$ which are probable candidates for superconductivity.

Composition	χ
$Pb_2Ba_2CaCu_2O_8$	2.537
$Tl_2Sr_2CaCu_2O_8$	2.531
$Tl_2Sr_3Cu_2O_8$	2.529
$Pb_2Sr_3Cu_2O_8$	2.543
$Pb_2Ca_3Cu_2O_8$	2.547

within the range of the known oxide superconductors which we have discussed so far. These are listed in Table III.

III. RESULTS AND DISCUSSION

Using the idea of electronegativity we have been able to explain successfully the pressure-induced superconductivity in elemental metals. We hope that it is also possible to explain pressure-induced superconductivity in nonmetals using the same reasoning. But in the case of a nonmetal such as Si the bonds will be broken at high pressures and the electrons will be delocalized which will drastically affect the value of Z_{eff} that has been used in the expression for χ.

Studies on oxide superconductors make us to claim that one of the criteria for an oxide material to be a superconductor is that its average electronegativity should be in the range 2.5–2.65. The converse is not necessarily true. We have cited the case of $La(Mg_{0.5}Nb_{0.5})O_3$. Further, it should be noted that all lanthanide elements have the same electronegativity so substitution of Y by all lanthanide elements will give the same χ value in the case of $YBa_2Cu_3O_7$. So problems arising with regard to achieving high T_c with Ce or Pr substitution in the place of Y cannot be explained by this simple approach. Similarly, this analysis which uses the concept of electronegativity which is purely of chemical origin will not be able to differentiate between La_2CuO_4 and La_2NiO_4 even though the latter exhibits magnetic excitations. This is due to the simple fact that Cu and Ni possess the same electronegativity value.

We would like to add that the range that we have prescribed for the average electronegativity for oxide superconductors will not be altered much because of the fact that Cu and O exist in different oxidation states. It is known that the value of χ for Cu^{1+} and Cu^{2+} are 1.9 and 2.0, respectively.[9] The variations with respect to oxygen's oxidation state are also small and since we are determining the average value of χ in a system of 13 atoms these effects will hardly affect our conclusion. A similar explanation holds good when Ba and/or Sr substitution is made in the case of La compounds and also for oxygen concentration variation in 1:2:3 systems. Since we are calculating only the average χ values, the above effects produce very little change in χ. The average χ values for pure La_2CuO_4 and for the composition $La_{1.8}Sr_{0.2}CuO_4$ are 2.657 and 2.648, respectively. Similarly, the values of average electronegativity are 2.58, 2.54, and 2.50 for O_7, $O_{6.5}$, and O_6, respectively, in the case of $YBa_2Cu_3O_{7-\delta}$. Normally, one would expect an abrupt change in the electronegativity value since dramatic changes in the properties occur for $O_{6.5}$. However, it is obvious that from the nature of our calculations these effects cannot be brought about. Based on our work we have also suggested the compositions which could be probable superconductors.

The underlying physics behind the range of electronegativity possessed by oxide superconductors is not difficult to understand. It has been stated earlier that $\chi=2$ can be approximately taken as the demarcation point that divides elements into metals and nonmetals. The fact that the value of oxide superconductors is centered around 2.6 indicates that they are poor metals and it is well known that poor metals are good superconductors. If this argument could be pushed further then flourinated compounds should be expected to be good superconductors as flourine is a superhalogen having an electronegativity of 3.9 in contrast to oxygen which has a value of 3.5. Another point to be noted is that the constancy of χ for all oxides, whether it is NbO or $Tl_2Ba_2Ca_2Cu_3O_{10}$, can be taken to be an indication that superconductivity in all materials may be only of electronic origin. The former compound consists of lighter Nb ions whereas the latter ones have heavier ionic masses and it seems as if the lattice vibrations are unimportant.

ACKNOWLEDGMENTS

One of the authors (R.A.) is thankful to Professor N. Kumar, Professor K. S. Singwi, and Dr. C. M. Varma for the valuable discussions. He also thanks Professor S. K. Joshi and Professor G. V. Subba Rao for their encouragement. Useful suggestions given by Dr. M. A. Subramanian, Dr. R. Suryanarayanan, and Dr. Shaukat Ali are acknowledged. He would also like to express his gratitude to Professor Abdus Salam for hospitality at International Centre for Theoretical Physics, Trieste, Italy, where part of the work was done. The authors acknowledge with thanks, the financial assistance given by the University Grants Commision, New Delhi, India.

*Present address: Physics Department, West Virginia University, Morgantown, WV 26506.

[1]C. C. Torardi, M. A. Subramanian, J. C. Calabrese, J. Gopalakrishnan, E. M. McCarron, K. J. Morrissey, T. R. Askew, R. B. Flippen, U. Chowdhry, and A. W. Sleight, Phys. Rev. B **38**, 225 (1988).

[2]Qi-Guang Luo and Rong-Yao Wang, J. Phys. Chem. Solids, **48**, 425, (1987).

[3]J. Wittig, in *Physics of Solids Under High Pressures,* edited by J. S. Schilling and P. W. Shelton (North-Holland, Amsterdam, 1981), p. 283.

[4]M. Rajagopalan, R. Asokamani, N. Vasavi, and G. Subramaniam, J. Low Temp. Phys. **66**, 169 (1987).

[5]R. Asokamani, T. N. B. Noorjahan, S. Pauline, and M. B. Suvasini, High Temp. High Pressure **18**, 113 (1986).

[6]G. Subramaniam, V. Sundararajan, S. Mathi Jaya, and R. Asokamani, High Temp. High Pressure **19**, 653 (1987).

[7]R. Asokamani, M. Rajagopalan, M. B. Suvasini, and V. Sundararajan, Phys. Rev. **33**, 7556 (1986).

[8]M. Rajagopalan, N. Vasavi, G. Subramaniam, and V. Sundararajan, and R. Asokamani, High Temp. High Pressure **18**, 389 (1986).

[9]Pauling, *The Nature of Chemical Bond* (Cornell Univ. Press, Ithaca, New York, 1960), p. 93.

[10]W. Gordy, Phys. Rev. **69**, 604 (1946).

[11]R. T. Sanderson, *Chemical Periodicity* (Van Nostrand Rein-

hold, New York, 1961), p. 37.
[12]P. Villars and J. C. Phillips, Phys. Rev. B **37**, 2345 (1988).
[13]J. M. Vandenberg and B. T. Matthais, Proc. Nat. Acad. Sci. U.S.A. **74**, 1336 (1977).
[14]D. C. Johnston, H. Prakash, W. H. Zachariassen, and R. Viswanathan, Mater. Res. Bull. **8**, 777 (1973).
[15]L. E. Toth, J. Less-Common. Met. **13**, 129 (1967).
[16]H. F. Braun and C. V. Segre, Solid State Commun. **35**, 735 (1980).
[17]H. F. Braun and C. V. Segre, Solid State Commun. **35**, 923 (1980).
[18]J. P. Remeika, G. P. Espinosa, A. S. Copper, H. Barz, J. M. Rowell, D. B. Whar, J. M. Vandenberg, D. E. Moncton, Z. Fisk, L. D. Wolfe, H. C. Hamaker, M. B. Maple, G. Shigane, and W. Thomson, Solid State Commun. **34**, 923 (1980).
[19]H. Barz, Mater. Res. Bull. **15**, 1489 (1980).
[20]P. C. Danohue and P. E. Bierstedt. Inorg. Chem. **8**, 2698 (1969).
[21]G. P. Meisner, Physica B **108**, 763 (1981).
[22]B. T. Matthais, M. Marezio, E. Corenzwit, A. S. Cooper, and H. Barz, Science **175**, 1465 (1972).
[23]M. Sergent, D. Fischer, K. Ecrouse, C. Perrin, and R. Chevrel, J. Solid State Commun. **22**, 87 (1975).
[24]R. Chevrel, M. Sergent, and M. Prigen, J. Solid State Commun. **3**, 515 (1972).
[25]G. V. Subba Rao and G. K. Shenoy, in *Current Trends in Magnetism,* edited by N. S. Satyamurthy and Madhava Rao (Indian Physics Association, Bombay, India, 1981).
[26]S. K. Sinha, G. W. Crabtree, D. G. Hinks, and H. Mook, Phys. Rev. Lett. **48**, 950 (1982).
[27]M. Ishikawa, M. Sergent, and O. Fischer, Phys. Lett. A **82**, 30 (1981).
[28]*F. S. Glasso, Structure Properties and Preparation of Perovskite Type Compounds* (Pergamon, Oxford, 1969), p. 60.
[29]A. W. Sleight, J. L. Gillson, and P. L. Bierstedt, Solid State Commun. **17**, 27 (1975).
[30]D. C. Johnston, J. Low Temp. Phys. **25**, 145 (1976).
[31]R. J. Cava *et al.*, High T_c Update **2** (10), 1 (1988).
[32]H. Takagi, S. Uchida, K. Kitazawa, and S. Tanaka, Jpn. J. Appl. Phys. **26**, L123 (1987).
[33]C. C. Torardi, M. A. Subramanian, J. C. Calabresse, J. Gopalakrishnan, K. J. Morrisey, T. R. Askew, R. B. Flippen, V. Chowdhry, and A. W. Sleight (unpublished).
[34]M. K. Wu, J. R. Ashburn, C. J. Torng, P. H. Hor, R. L. Meng, L. Gao, A. J. Huang, Y. O. Wang, and C. W. Chu, Phys. Rev. Lett. **58**, 908 (1987).
[35]R. J. Cava *et al.*, High T_c Update **2** (22), 1 (1988).
[36]D. E. Morris, High T_c Update **2** (22), 1 (1988).