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A Remark Concerning the Possibility of Getting Better Superconductors

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Abstract. It is suggested that $Nb_3Ge_xMg_{1-x}$ with $x \simeq \frac{2}{3}$ (if it exists in the A-15 phase) is a better superconductor than Nb_3Ge. This is corroborated by a LCAO calculation of the band structure and density of states function.

The connection between the superconductivity transition temperature T_c and band structure was first formulated in the BCS theory [1]. There, T_c was explicitly related to $N(0)$, the density of states at the Fermi level. In the strongly coupled superconductors the BCS model fails and a better approximation such as McMillan's [2] is needed. This approximation gives a numerical relationship between the superconducting transition temperature T_c to the Debye temperature θ_D, the electron mass renormalization λ, and the coulomb pseudopotential μ^*. The important factor is λ, which can be approximately expressed in terms of electron and phonon properties:

$$\lambda = \frac{N(0)\langle I^2\rangle}{M\langle\omega\rangle/\langle\omega^{-1}\rangle}$$

where $\langle I^2\rangle$ is a double average over the Fermi surface of the squared electron phonon matrix, M is the ion mass, and $\langle\omega^m\rangle$ is the mth moment of the phonon spectrum. It was shown by McMillan that $N(0)\langle I^2\rangle$ is roughly constant for many transition metals and alloys, and thus the variations in λ are mainly determined by the phonon spectrum.

In the high T_c compounds V_3X and Nb_3X, an extremely narrow peak in the density of states near the Fermi level is found, both experimentally [3] and theoretically [4]. In such materials the phonon spectrum depends on $N(0)$ due to electron 'dressing' of the phonons [5]; a high density of states causing phonon softening, thus even in McMillan's formalism T_c may depend on $N(0)$. Fradin and Williamson showed recently [6] that a reasonably good account for the dependence of λ in the V_3X compounds on the composition expressed by X, is given by:

$$\lambda = \frac{\lambda_0}{1 - N(0)B}$$

where λ_0 and B are constants. This gives essentially the following dependence of T_c on $N(0)$:

$$T_c \propto \exp\left(\frac{N(0)B}{\lambda_0}\right)$$

Thus T_c is strongly dependent on $N(0)$.

The intermetallic compounds Nb_3X and V_3X, all having the A-15 structure are the best known superconductors [7]. The high value of T_c in these compounds is attributed by some authors [6, 8] to the high density of states at the Fermi level. A simplified linear chain model was suggested for the band structure [9] and carried out further by Labbé, Friedel and Barisic [10] accounting for some electronic anomalies and for the high T_c. In this model the narrow peak at E_F is attributed to the δ bands (d_{xy}, $d_{x^2-y^2}$ for chains in the z direction). The difficulty encountered by the linear chain model is that it requires the next-nearest-neighbours interaction to be very small compared to nearest-neighbours interaction. This assumption was shown to be wrong [11]. Taking into account the full inter-chain interaction it was shown that $\delta_2(d_{xy})$ as well as $\pi(d_{xz}, d_{yz})$ bands might contribute to the high density of states at E_F [4, 12]. Furthermore, the measurement of the nonaxially symmetric component η of the quadrupole tensor ($\eta \simeq 0.12$ for V_3Si in the tetragonal phase) indicates a strong π component in the density of states at E_F [13], [17].

The density of states function of the d band has some peaks in the vicinity of the Fermi level. Nonselfconsistency, the one electron approximation, as well as inaccuracies in the calculation of the TB integrals may cause inaccuracies of the order of 50 mRy in V_3X and 100 mRy in Nb_3X [12]. Thus it is impossible to identify the symmetry of the peaks to within better than about 50 mRy of E_F from a first principles calculation, without any critical experiment. The influence of the X-atoms on the band structure and the related physical anomalies can be studied only in a calculation which takes into account mixture between the d and X $-$ p bands (the X $-$ s band was found to have only small effect on the d band [14], and thus it is ignored here). In such a calculation a special peak, of the symmetry Γ_{15} is found, which is hybridized quite strongly with the X $-$ p band. For Nb_3Ge (as well as for the V_3X compounds with X = Si, Ga, Ge, etc. [4]) this peak is found to lie below E_F when admixture with the Ge $-$ $4p$ band is ignored. But it is pushed above E_F when such an admixture is allowed. The special character of this peak is its very high sensitivity to the X $-$ p band. Regarding the high T_c of Nb_3Ge and the strong dependence of T_c on $N(E_F)$, one could expect to get a better superconductor by raising $N(E_F)$. This could possibly be done by shifting the Γ_{15} peak of Nb_3Ge till it coincides with the Fermi level. A possible way to do it is to interchange some of the germanium atoms with other atoms, whose p band lies above the Fermi level. We describe here a 'full' TB calculation showing the band structure of such a material, as yet hypothetical, namely $Nb_3Ge_xMg_{1-x}$. The calculation concentrates on the Nb $-$ $4d$ band and its interaction with the X $-$ p band. Table I summarizes the TB parameters needed for such a calculation. The notations and method of calculation were described in detail elsewhere [4, 14]. The main sources for the inaccuracies involved in such a calculation as presented here are the following: (i) Nonselfconsistency: the various parameters are estimated using atomic functions and potentials. Moreover, all the wave functions belonging to the same band have the same radial wave function [15]. This causes on the average inaccuracies of the order of 50–100 mRy for Nb_3X. (ii) The neglect of 3-center integrals

Table I

The crystal field integrals, transfer integrals and overlap integrals for the Nb $-$ d band and X $-$ p band (X = Ge, Mg, Au). $x_1 = \frac{a}{2}$, $x_2 = \frac{\sqrt{6}}{4}a$, $x_3 = \frac{\sqrt{5}}{4}a$, $x_4 = \frac{\sqrt{3}}{2}a$. (The center of gravity of the d band is at $E = 0$).

		Interaction parameters (energies in mRy)			Overlap parameters		
Crystal Field Integrals	$K\sigma$	-180					
	K_π	-10					
	K_{δ_1}	110					
	K_{δ_2}	40					
	K_p(Mg)	450					
	K_p(Ge)	-700					
	K_p(Au)	550					
	K_p(Be)	200					
Intra d-band Integrals	$dd\sigma(x_1)$	-150			0.07		
	$dd\pi(x_1)$	160			-0.15		
	$dd\delta(x_1)$	-55			0.08		
	$dd\sigma(x_2)$	-85			0.06		
	$dd\pi(x_2)$	70			-0.12		
	$dd\delta(x_2)$	-18			0.05		
X $-$ X $-$ p intra band Integrals	$pp\sigma(x_4)$	50			0		
	$pp\pi(x_4)$	0			0		
	X =	Ge	Mg	Au	Ge	Mg	Au
X $-$ p, Nb $-$ d Interband Integrals	$dp\sigma(x_3)$	-140	52	-50	0.115	-0.023	0.020
	$dp\pi(x_3)$	96	-85	85	-0.140	0.136	-0.132

gives rise to inaccuracies of 10–20 mRy. (iii) Neglecting terms which contain the energy of the atomic level and which should be taken into account when overlap is considered. Schematically, one has to solve the equation

$$|H - \epsilon S| = 0$$

where H and S are the Hamiltonian and overlap matrices respectively. If, for example, the d band is considered, terms like $S\Delta$ appear, where Δ is the difference between the energy of the atomic d level and the center of gravity of the d band. These terms are effectively added to the transfer integrals. For the $4d$ band of Nb_3X it is found that $\Delta \simeq 50$ mRy and the relative change of the effective transfer integrals is of the order of 10%. For the dp interaction, again the zero energy can be taken into account in the same manner, but now $\Delta = |E_d^{at} - E_p^{at}$. For the $Nb_3Mg_xGe_{1-x}$ system $\Delta \simeq 0.1$ Ry and the relative changes of the effective transfer integrals are about 10–20%. For the V_3Si system $\Delta = |E_d^{at} - E_p^{at}| \simeq 0.35$ Ry and the terms containing Δ should be added. In all the calculations presented here these terms are omitted, causing inaccuracies of the order of 20–30 mRy. Regarding the total inaccuracies, the results presented below should be considered as semiquantitative only.

Figure 1 gives the calculated energy levels at the high symmetry points of the Brillouin zone. The influence of the X-atoms is shown by comparing the energy levels

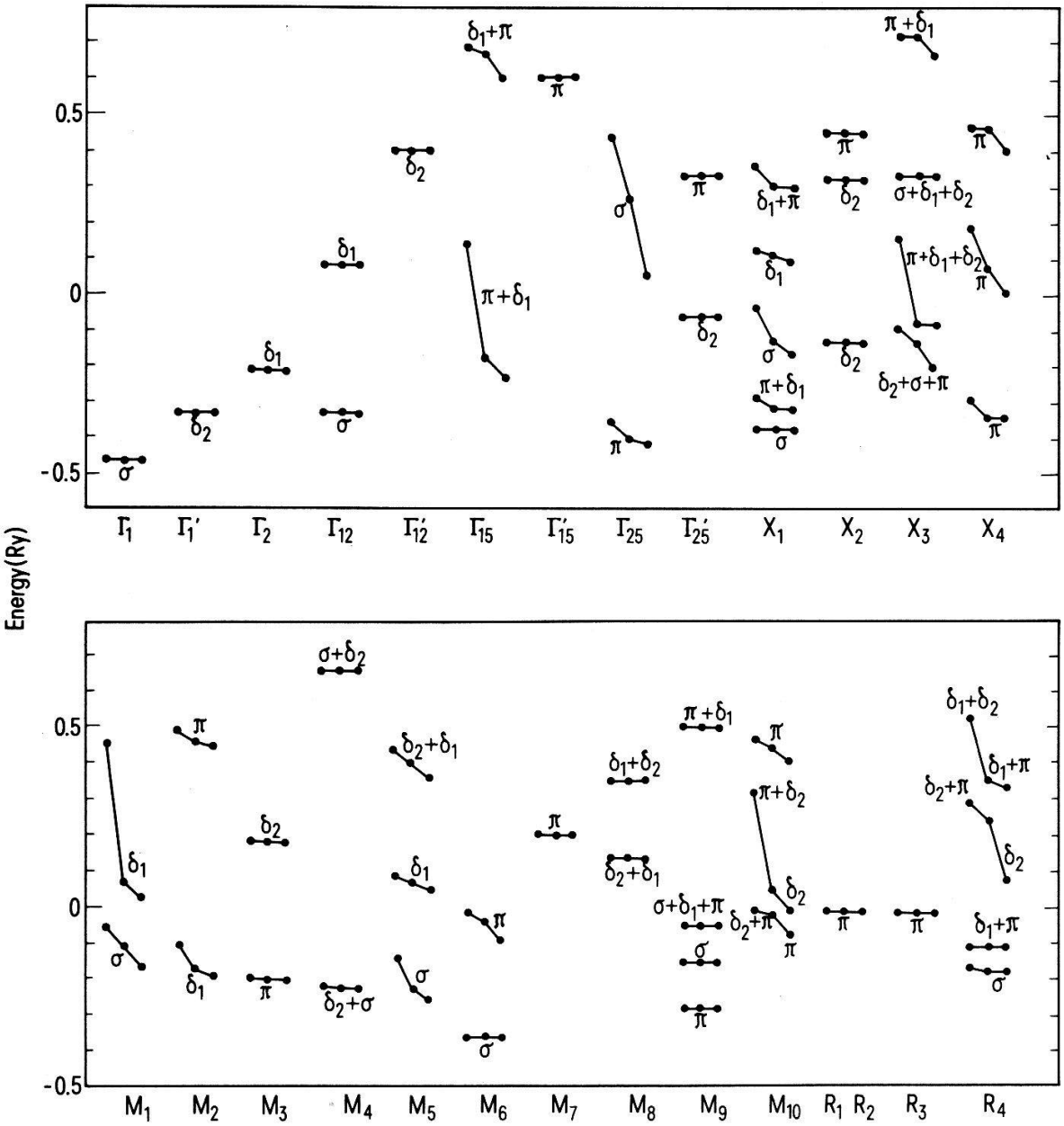

Figure 1
Comparison of energy levels of the Nb — *d* band at high symmetry points of the BZ, calculated for Nb_3 (in the center) and for Nb_3Ge (on the left) and for Nb_3Mg (on the right).

for Nb_3Ge, Nb_3Mg and the hypothetical Nb_3 (where the X-atoms were taken out). In the following figures the density of states is calculated for Nb_3Ge and Nb_3Mg and the mixed compound $Nb_3Ge_{2/3}Mg_{1/3}$. For $Nb_3Ge_{2/3}Mg_{1/3}$ we assumed weighted averages of the TB parameters. Besides the inaccuracies inherent in the method of calculation, the results presented here lack sufficient numerical precision. Every calculation of the density of states function takes about four hours on a CDC-6400 computer, and thus we could not enlarge the density of the mesh in the Brillouin zone. A maximum in the density of states should occur when the $\Gamma_{15}(\pi + \delta_1)$ peak coincides with the $\Delta_5(\delta_2 + \pi)$ peak. Unfortunately, an 'experimental' determination of x in $Nb_3Ge_{1-x}Mg_x$ that would yield such a coincidence requires computer time which is beyond our resources; moreover, the accuracy is not sufficient such that a more precise determination of x would be meaningful. From Figure 4 it appears, that when the two

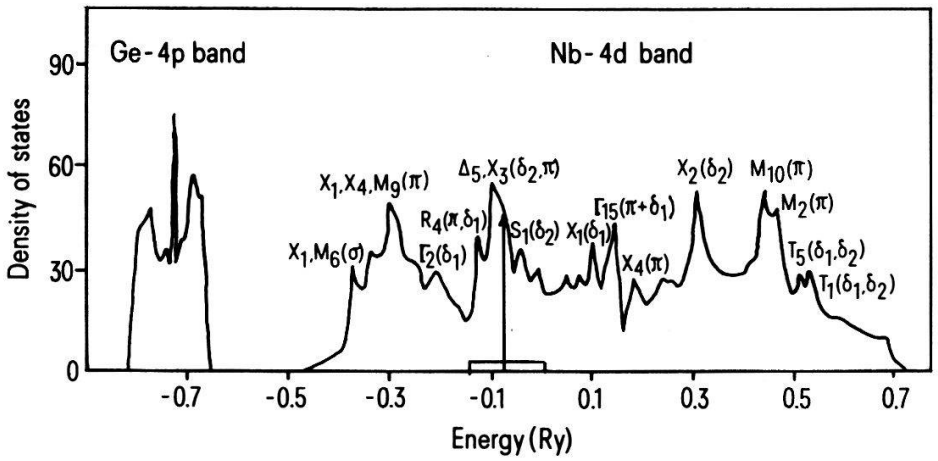

Figure 2
Density of states curve (in states/unit-cell/Ry/spin) calculated for Nb_3Ge. E_F is given by the arrow and the uncertainty in E_F is given by the shaded area.

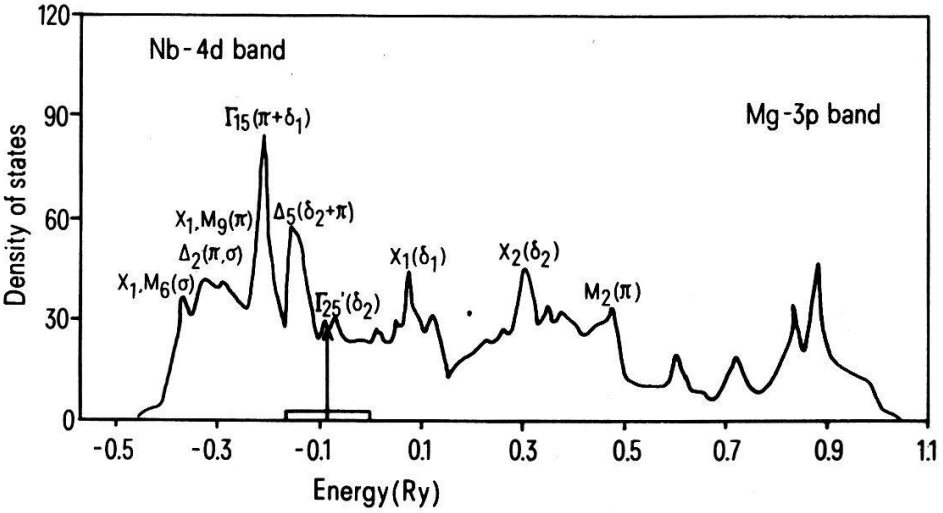

Figure 3
Density of states curve (in states/unit-cell/Ry/spin) calculated for Nb_3Mg.

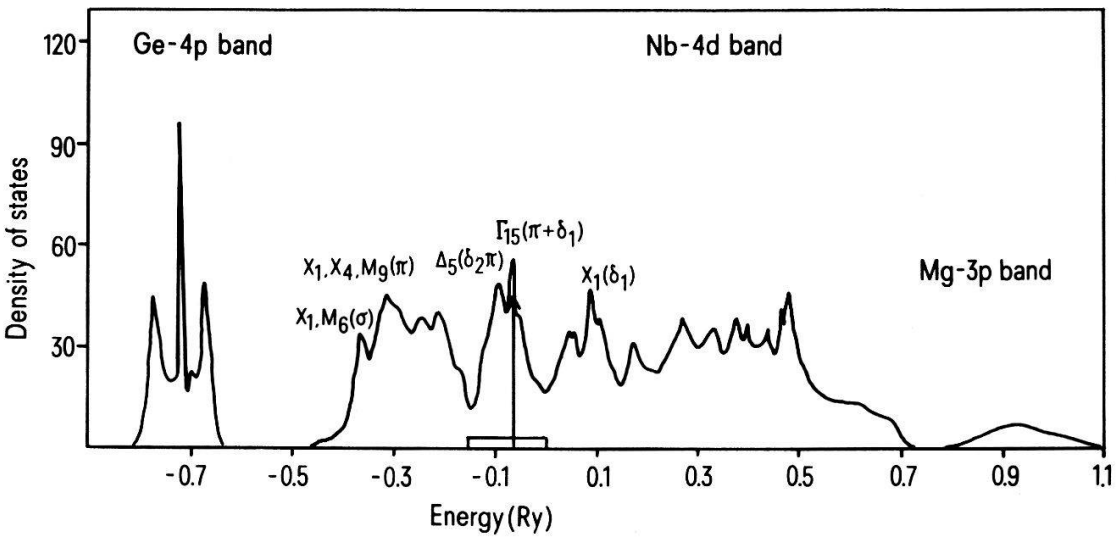

Figure 4
Density of states curve (in states/unit-cell/Ry/spin) calculated for $Nb_3Ge_{2/3}Mg_{1/3}$.

peaks coincide, the density of states may increase by 20%, very roughly. Regarding the high sensitivity of T_c to $N(E_F)$, it is not unreasonable that during a continuous change of the Mg concentration an optimum can be found, for which T_c would be maximum.

$Nb_3Ge_xMg_{1-x}$ should be difficult to prepare by standard melting techniques (such as arc furnace, induction furnace) because of the low boiling point of Mg. However, by sputtering it should be possible to prepare films of this compound, if it exists at all in the A-15 phase. Other alternatives are $Nb_3Ge_xAu_{1-x}$ and $Nb_3Ge_xBe_{1-x}$. In both cases the X-atom p level is higher than in Nb_3Ge. In the gold compound, the gold tends to be located on the nioboum (chain) sites [16]; in the berillium compound, the $X - p$ level is apparently not high enough. Extensive research to find materials with a high $X - p$ band and a well-ordered A-15 phase may be required to verify (or refute) the present suggestion.

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