RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 47, NUMBER 17 1 MAY 1993-I

Internal electric fields and resonant Fermi-level pinning in anionic metals

J. C. Phillips
AT&T Bell Laboratories, Murray Hill, New Jersey 07974

(Received 11 February 1993)

In the normal Jahn-Teller effect a molecular distortion at low temperatures reduces total energy by splitting electronic states which are highly degenerate at the Fermi energy. Thomas *et al.* have discovered in layered Bi_2Te_3:Bi an anti-Jahn-Teller effect in the density of conduction electrons, which effectively doubles between room and low temperatures. This effect is explained by the presence of large internal electric fields induced by dopant configurational distortions which are screened by resonant states pinning the Fermi level. Such states have been supposed previously to be the novel electronic mechanism responsible for high-temperature superconductivity in the layered cuprates.

I. INTRODUCTION

Fermi-level pinning by structural defects or impurities is a characteristic feature of metal-semiconductor interfaces.[1] Anionic metals, especially those that contain two or more metallic elements and oxygen or a chalcogenide anion, are the materials that form the basis of high-temperature superconductors such as the $(Ba,K)(Pb,Bi)O_3$ perovskites and the many-layered cuprate pseudoperovskites. Each of these compounds can be imagined to consist of a semiconductor building block (such as BaO) combined with a metallic building block (such as BiO_2) on an atomic scale. Ordinarily these combinations are insulating and they must be doped to become metallic. High-temperature superconductivity occurs in these materials just on the metallic side of the metal-semiconductor transition, and T_c may decrease or vanish if the material becomes heavily metallic,[2] as in well-annealed $La_{2-x}Sr_xCuO_4$ for $x \gtrsim 0.21$. Thus it is not enough to dope the semiconductive layers and make them metallic, but also the local environment of the dopants must be favorable. This is consistent with the idea of resonant pinning of the Fermi level by the dopants, with the pinning disappearing when the dopant concentration is too high. These ideas have been developed at length by me elsewhere,[3] and they explain a great many experimental results which are not easily understood in homogeneous or mean-field models which omit resonant pinning and which treat the dopants as randomly distributed rather than arranged in specific geometries.

One of the central questions that arises in the resonant-pinning model[3] is whether or not this is accidental. One could argue that by trial and error experimentalists have adjusted the resonant states so that some of them do indeed pin E_F. The adjustment may involve dopant short-range order, and it can occur even in simple systems, such as Cu-Zn alloys (brass), where second-neighbor Zn pairs pin E_F at low Zn concentrations.[3] However, the dramatic effect of high-temperature superconductivity occurs only in anionic multinary metals containing metal-semiconductor building blocks which are vicinal to ferroelectrics on quantum structural diagrams.[4] Moreover on these diagrams the Chevrel chalcogenide superconductors and the perovskite-pseudoperovskite alloys lie on opposite sides of the ferroelectric compounds, and all have very similar values of ΔR, a suitably averaged cation-anion quantum size difference. This suggests that there are strong internal electric fields in the anionic metals similar to the internal fields of ferroelectrics. Metallic screening of these fields lowers the total energy by $-\sigma E_i^2$, where E_i is an internal field and σ is a dielectric polarizability. Resonant pinning greatly enhances σ, and we can imagine that if the energy U_{JT} which can be gained from Jahn-Teller distortions is small, then rather than split the pinning band into bonding and antibonding states, lower total energy will be obtained by resonant screening.

This scenario, as stated, is very simple in the context of basic physical principles, but its actual application to anionic metals in practice is very complex. These metals have complex structures with three or more elements and many inequivalent sites per unit cell, which render experimental determination of defect configurations quite difficult. Apart from global quantum structural diagrams,[4] which are quite suggestive, we have little direct evidence for resonant Fermi-energy pinning. Most of the data suggest[2] that dopant activity is enhanced near domain walls, where one would expect to find larger internal piezoelectric fields. Also the differences between Debye-Waller factors measured by diffraction and by ion channeling[5] is large, especially near T_c, which implies failure of mean-field models to recognize spatial inhomogeneities near active dopants. Such inhomogeneities apparently lead to inhomogeneous buckling of CuO_2 planes in the layered cuprates.[6] Thus there are some regions which are Jahn-Teller distorted and some which are not, presumably because of overall constraints (cage effects) associated with the lattice as a whole.[7] Because of these cage effects one can have much larger values of $N(E_F)$ locally in perovskites and pseudoperovskites than in simple metals, and hence much larger values of the electron phonon coupling constant $\lambda = N(E_F)V$ (where V is an electron-phonon matrix element of order the band width $W \sim 2$ eV) than in simple metals.

The foregoing discussion outlines some of the evidence for structural inhomogeneities associated with electrically active dopants which resonantly pin E_F. It is evidently complex and the uncertainties associated with determination of the electronically active dopant fraction seem unavoidable. One would like to find simpler binary systems which exhibit resonant pinning which could be studied in more detail. Such a system appears to be Bi_2Te_3:Bi, where recent optical data[8] indicate a large enhancement of the active carrier density as the temperature is lowered. This is just the opposite of what one would expect from the Jahn-Teller effect, and it can be called an anti-Jahn-Teller effect which has arisen because of enhanced resonant pinning.

In this paper we discuss these data in considerable detail, using an approach which is quite different from that previously used.[8] The reader is forewarned that many of the materials complexities found in the multinary (pseudo) perovskites are still present in Bi_2Te_3:Bi and related doped binary compounds. In a way this is reassuring because it suggests that there is good reason to draw analogies between multinary HTSC materials and this binary material. However, most of the literature on these materials is based on powder samples, and we suspect that many of these samples may have been contaminated by oxygen, as was proved to be the case for the Chevrel compounds only after a decade of research on their superconductive properties.[9,10] The data[8] we discuss were obtained on single crystals grown by the Czochralski process and presumably have much lower levels of oxygen contamination. Nevertheless, many intrinsic uncertainties remain concerning the crystal chemistry of active dopants, and it is these that we wish to discuss.

II. CRYSTAL CHEMISTRY OF Bi DOPANTS IN Bi_2Te_3

The tetradymite structure of Bi_2Te_3 is rhombohedral with three $Te^{I}BiTe^{II}BiTe^{I}$ packs (layerings) per unit cell.[11] Many substitutional alloys are known with this structure, with Sb replacing Bi and/or Se or S replacing Te. The Te^{II} site is sixfold coordinated, while the Te^{I} site has three nearest neighbors.[12] Smaller and more electronegative[4] S occupies only Te^{II} sites,[10] but Bi is larger and more electropositive, so we would expect it to occupy a Te^{I} site. In fact the respective size ΔR and electronegativity ΔX differences are[4] $R(\mathrm{Te})-R(\mathrm{S})\sim R(\mathrm{Bi})-R(\mathrm{Te})$ and $X(\mathrm{S})-X(\mathrm{Te})\sim X(\mathrm{Bi})-X(\mathrm{Te})$. In the discussion of the optical data it was suggested[8] that because S occupies Te^{II} sites, Bi should also. However, this neglects the differences in the sign of ΔR and ΔX for the two sites in the two cases. These differences explain[11] why the energy gap for $Bi_2(Te_{1-x}Se_x)_3$ alloys peaks at $x=\frac{1}{3}$.

While the sequence $Te^{I}BiBiBiTe^{I}$ is symmetric, $BiBiTe^{II}BiTe^{I}$ is not, and in general the substitution of Bi on Te^{I} sites will generate dipole moments $\mathbf{p}$ normal to the layers. It is these dipole moments that produce the internal fields $\mathbf{E}_i$ mentioned in the Introduction. These fields are analogous to the ferroelectric fields generated by ferroelectric distortions in perovskite and pseudoperovskite HTSC. Thus in order to establish a close analogy between resonant pinning of E_F in the latter and in Bi_2Te_3:Bi it is important that Bi dopants occupy Te^{I} and not Te^{II} sites. The arguments given here for Te^{I} substitution, while plausible and fully consistent with crystal chemistry,[11] are still theoretical. For this reason it would be highly desirable to determine the Bi site experimentally, for instance, by Te Mössbauer spectroscopy.

III. ORIGIN OF TEMPERATURE DEPENDENCE OF METALLIC CHARGE DENSITIES

From the optical measurements of the effective plasma frequency ω_{Ps}, Thomas *et al.* inferred[8] that nm_e/m is S shaped as a function of T, saturating near 300 K at a value about half its $T=0$ limit. The midpoint of the curve occurs near $T=T_m=100$ K, which strongly suggests that the broadening of a resonant peak in $N(E)$ centered at or very near $E=E_F$ is occurring thermally. The low value of T_m is suggestive of van der Waals forces, such as might occur due to interactions between two $Bi_{[Te^{I}]}$ on vicinal layerings. The measured values of $\hbar\omega_{Ps}$ are of order 50 meV or $600k_B$, which is comparable to k_BT_m. This suggest that the self-consistent screening of internal electric fields associated with van der Waals distortions may alter the width Γ of the resonance in $N(E)$ pinning E_F and its effective polarizability.

Consider the following explicit Hamiltonian model. Let

$$\mathcal{H}=\mathcal{H}_{\mathrm{pr}}+\mathcal{H}_L\ , \tag{1}$$

where $\mathcal{H}_{\mathrm{pr}}$, the pinning resonance screening energy, is dependent on the pinning resonance width Γ, as follows:

$$\mathcal{H}_{\mathrm{pr}}=-n_iE_i^2[\Gamma^2+(kT)^2]^{-1/2}\ , \tag{2}$$

where E_i is the dopant ionization energy, and Γ is the width of the pinning resonance. The form of (2) is designed to reduce to a Curie-Weiss term as $\Gamma\to 0$ and to be independent of T when $\Gamma \gg kT$. It is the form one would expect if the random phase approximation is valid for thermally excited resonances. Note also that the strength of the unscreened dipolar fields associated with $Bi_{[Te^{I}]}$ dopants is fixed as $T\to 0$. The dopant resonant screening of these fields somewhat resembles an electrical analogue of screening of local magnetic moments (the Kondo effect); however, because exchange interactions are weak and short range, the Kondo temperature T_K is typically $\lesssim 10$ K, whereas here the characteristic temperature is $T_m\sim 100$ K. In oxides this temperature should be of order 200–300 K or more.

The lattice energy $\mathcal{H}_L$ has the double-well form typically used[13] to describe ferroelastic or ferroelectric distortions associated with a configuration coordinate w,

$$\mathcal{H}_L=E_0-E_2(w/a)^2+E_4(w/a)^4\ , \tag{3}$$

and a is an average van der Waals spacing. The double-well minima occur at

$$E=\mathcal{H}_L(w_0)=E_0-E_2^2/2E_4\ , \tag{4}$$

$$w_0^2=a^2E_2/E_4 \tag{5}$$

but in the present case we assume that $\Gamma=\Gamma(w)$ and specifically

$$\Gamma = g(n_i) E_i w / a \ . \tag{6}$$

The dimensionless numerical factor $g(n_i)$ depends on the dopant density n_i in a complex way. It may be of order $E_i E_2 / E_4^2$ when the dopant concentration is near the solid solubility limit. I suppose that E_i itself is $\lesssim 0.1$ eV (a deep trap energy) and that $E_2^2/2E_4$ is of order 100 K.

There are a good many parameters in this model, and I have presented it merely as a convenient way to describe the competition between the resonant screening electronic energy and a double-well lattice energy on a van der Waals (interlayer) scale. There is only one significant parameter in the measured electronic density nm_e/m as a function of T, and this is the midpoint at $T = T_m = 100$ K. At high temperatures $T \gg T_m$ the configuration coordinate w oscillates between both wells, Γ is large and n is small. At low temperatures ordinarily w would settle in one of the wells, $w = \pm w_0$, especially in ferroelectrics where this is favored by the Lorentz local field interaction, which is omitted from (1). Here, however, something different may happen. To minimize $\mathcal{H}_{\text{pr}}$ as $T \to 0$ one must minimize Γ and because of (6) this happens for $w = 0$. This in turn increases $n(E_F)$ which we suppose is given by

$$n(E_F) = n_0(E_F) + n_1(E_F) \Gamma_0^2 / (\Gamma_0^2 + \Gamma^2) \ , \tag{7}$$

where Γ_0 is the nonthermal pinning resonance width due to spatial inhomogeneities. In other words, self-consistent internal screening by pinning resonances can increase $n(E_F)$ as $T \to 0$, which is the "anti-Jahn-Teller effect" mentioned in the Introduction. In principle this entire model should be made self-consistent by connecting Eq. (7) with Eq. (2). Such a more quantitative treatment at present is unwarranted by the available data. The present model accomplishes its aim, which is to show how resonant screening can produce an anti-Jahn-Teller effect.

IV. CONCLUSIONS

The temperature-dependent carrier density $N(E_F)$ inferred from $\omega_{Ps}(T)$ by Thomas *et al.*[8] seems to represent the observation of the formation of resonant pinning states at $T \lesssim 100$ K in Bi_2Te_3:Bi. These states may be characteristic of anionic metals with large internal fields which exist because of perovskite ferroelastic instabilities or because of layer buckling. In the layered cuprates both kinds of instabilities may exist and may generate internal piezoelectric fields. The screening of these fields may enhance $n(E_F)$ and may generate the very high T_c's which characterize many-layered cuprate compounds.

We would expect in the layered cuprates that the temperatures T_m at which resonant pinning states form would be higher than in tellurides, say 300 K, instead of 100 K. It is also possible that in systems with extended defects, such as domain walls or compositional waves, that the paths followed by current carriers in an external magnetic field might be changed by the formation of such resonant states. Experimental data on the Hall effect in layered cuprates often yield a constant Hall carrier density $n_H(T)$ for $T \gtrsim 300$ K and a (roughly) linear freezeout, $n_H(T) \propto T$ at lower temperatures.[3] This freezeout may arise from temperature-dependent screening in the presence of inhomogeneous internal piezoelectric fields near domain walls.[3]

One of the principal objections to my model of resonantly enhanced T_c's in the layered cuprates has been that in a metal such pinning resonances would be removed by Jahn-Teller distortions. I have previously pointed out that the "cage" constraints imposed by layering represent an ideal way to avoid the Jahn-Teller effect.[7] The Bi_2Te_3:Bi structure carries this argument one step further: if Bi occupies Te^I sites, then the geometry of the host lattice automatically generates electric dipole moments even when the formal charge state of the dopant is neutral, and this is what makes possible the enhancement of $n(E_F)$ at low temperatures. Note that this mechanism does not require dopant ionization. It represents an attractive alternative to the often-discussed mechanism of charge transfer, for example, between CuO_2 planes and CuO_{1-x} chains in $YBa_2Cu_3O_{7-x}$. Finally, it is striking that as experimental evidence accumulates on the microscopic electronic structure of anionic metals, it is tying up the "loose ends" of the resonant pinning model. Many other similar examples are discussed elsewhere.[3]

Recently, powerful evidence that Fermi-level resonant point defects may exist in $(Bi,Pb)_2 Sr_2Ca_2Cu_3O_{10}$ has been obtained by Eibl using high resolution electron microscopy.[14] There are two kinds of Cu sites in this layered cuprate, in the central planar CuO_2 layer and the outer pyramidal layers. A high fraction (~25%) of the central Cu and O sites appear to be vacant. In this oxide case the background dielectric screening is much smaller than in Bi_2Te_3 and the internal electric fields are accordingly much larger. Thus there may be considerable Fermi-level pinning in the central layer. The 2:2:2:3 phase appears to be essentially a surface phase associated with grain boundaries with $T_c \sim 110$ K. The enhancement in T_c compared to 2:2:1:2 (85 K) is presumably due to the central layer and may be associated with resonant pinning. Given the inherent complexities of defect configurations in metastable phases, the correspondence between these data and the general structural model discussed previously[3] is quite remarkable.

---

[1] R. E. Allen and J. D. Dow, Phys. Rev. B **25**, 1423 (1982); C. H. Chen, D. J. Werder, S.-W. Cheong, and H. Takagi, Physica C **183**, 121 (1991).

[2] H. Takagi *et al.*, Phys. Rev. Lett. **68**, 3777 (1992).

[3] J. C. Phillips, Phys. Rev. B **40**, 7348 (1989); **45**, 12 647 (1992); **46**, 8542 (1992).

[4] K. M. Rabe, J. C. Phillips, P. Villars, and I. D. Brown, Phys. Rev. B **45**, 7650 (1992).

[5] R. P. Sharma, F. J. Rotella, J. D. Jergensen, and L. E. Rehn, Physica C **174**, 409 (1991), see Fig. 7.

[6] M. Arai *et al.*, Phys. Rev. Lett. **69**, 359 (1992); S. J. L. Billinge and T. Egami (unpublished).

[7] J. C. Phillips, Phys. Rev. B **40**, 8774 (1989).
[8] G. A. Thomas *et al.*, Phys. Rev. B **46**, 1553 (1992).
[9] D. W. Capone, R. P. Guertin, S. Foner, D. G. Hinks, and H. C. Li, Phys. Rev. Lett. **51**, 601 (1983); Phys. Rev. B **29**, 6375 (1984).
[10] J. C. Phillips, J. M. Vandenberg, and K. M. Rabe, Europhys. Lett. **18**, 349 (1992).
[11] F. Hulliger, *Structual Chemistry of Layer-Type Phases* (Reidel, Boston, 1976), pp. 196–201; J. R. Drabble and C. H. L. Goodman, J. Phys. Chem. Solids **5**, 142 (1988).
[12] J. L. C. Daams, P. Villars, and J. H. N. Vucht, *Atlas of Crystal Structure Types for Intermetallic Phases* (ASM, Materials Park, OH, 1992), p. 5906.
[13] J. M. de Leon, D. Conradson, I. Batistić, and A. R. Bishop, Phys. Rev. B **46**, 5466 (1992).
[14] O. Eibl, Physica C **184**, 93 (1991). Regrettably I was unfamiliar with this paper when Ref. 3 was written.