Missing Valence States, Diamagnetic Insulators, and Superconductors

C. M. Varma
AT&T Bell Laboratories, Murray Hill, New Jersey 07974

(Received 8 July 1988)

About fifteen elements in the periodic table skip certain valences in all the compounds they form. This is understood to arise from a negative effective intra-atomic interaction. A model with such interactions as well as interatomic repulsions gives insulating behavior near half-filling and superconductivity farther from it in agreement with the properties of $BaPb_xBi_{1-x}O_3$ and $Ba_xK_{1-x}BiO_3$.

PACS numbers: 74.10.+v, 74.65.+n

The compounds of Ga, In, and Tl form with the formal valence states +1 and +3, of Ge, Sn, and Pb with +2 and +4, and of Bi and Sb with +3 and +5. Also Ti forms in +2 and +4 states and V and Nb in +3 and +5 states. The intermediate valence states are either unstable or metastable. It is commonplace to say that the valence states found are such as to give the stable closed-shell configurations. It seems to us worthwhile to incorporate the microscopic physics behind this phenomena in a model which could then be used for other calculations.

This matter is of considerable current interest. According to band theory the compound $BaBiO_3$ (Refs. 1-4) should be a metal but it is a diamagnetic insulator. The average formal charge state of Bi is +4, or one electron outside a closed shell. If Bi^{4+} were allowed, the insulating ground state of this compound would have spin $\frac{1}{2}$ at Bi sites and be antiferromagnetic, (AFM), which it clearly is not. Thus $BaBiO_3$ is not a Mott insulator either. On moving away from half-filling by the substitution of Bi with Pb, superconductivity with $T_c \approx 12$ K is found[1-4] near the metal-insulator boundary; the substitution of Ba with K or Rb produces T_c near 30 K.[5] Considering the meager density of electronic states near the Fermi energy estimated for these compounds,[5] we know that such high T_c's are unlikely from the conventional electron-phonon mechanism. It is of interest to ask whether the high T_c is also related to the physics which leads to valence skipping.

Phenomenological model Hamiltonians of the Hubbard type give rise to valence skipping provided the onsite interaction energy is attractive and comparable or larger than the kinetic energy.[6] Since the attractive Hubbard model has either an insulating (charge disproportioned) or a superconducting ground state (at half-filling), the connection between superconductivity and valence skipping is apparent.

One can generate "negative-U" interactions by eliminating phonons if the electron-phonon coupling is strong enough. But valence skipping is ubiquitous for the elements named above irrespective of the other elements involved. It is therefore natural that it be mostly related to electronic properties of the elements.

We have constructed in Table I the effective intra-atomic repulsion energy U_n for the charge state $+n$ from the measured ionization energies of the elements.[7] U_n is defined as

$$U_n = (E_{n+1} - E_n) + (E_{n-1} - E_n) , \tag{1}$$

where E_n is the total energy of the atom in the nth charged state. U_n of most elements increases as n increases, reflecting the smaller size of the orbitals for larger n. For the valence skippers it has a minimum at

TABLE I. Bare intra-atomic repulsion parameters U for several elements that skip valence in compounds. U for the skipped valence as well as for the stable valences on either side of it are calculated from the measured ionization energies (Ref. 7).

Bi	$U_{3+} = 19.7$ $U_{4+} = 10.7$ $U_{5+} = 32.3$	Sb	$U_{3+} = 18.8$ $U_{4+} = 11.9$ $U_{5+} = 52.0$		
Pb	$U_{2+} = 16.9$ $U_{3+} = 10.4$ $U_{4+} = 25.5$	Sn	$U_{2+} = 15.9$ $U_{3+} = 9.1$ $U_{4+} = 31.6$	Ge	$U_{2+} = 18.2$ $U_{3+} = 9.5$ $U_{4+} = 48.7$
Tℓ	$U_{1+} = 14.3$ $U_{2+} = 9.4$ $U_{3+} = 20.9$	In	$U_{1+} = 13.1$ $U_{2+} = 9.2$ $U_{3+} = 26.4$	Ga	$U_{1+} = 14.6$ $U_{2+} = 9.2$ $U_{3+} = 26.4$
Nb	$U_{3+} = 13.3$ $U_{4+} = 11.7$ $U_{5+} = 53.0$	V	$U_{3+} = 18.7$ $U_{4+} = 17.0$ $U_{5+} = 64.0$	Ti	$U_{2+} = 13.9$ $U_{3+} = 15.8$ $U_{4+} = 56.6$

the valence that is skipped. This reduced value of course reflects the larger correlation energy of closed electronic shells with respect to open shells. In the ensuing discussion we will take this as given.

The U for the missing valence state in Table I is small but not negative. This is, however, not the U to be used in a model for a solid which contains only the s orbitals for the metal atoms. As argued by Herring[8] for the case of transition metals the appropriate U should be screened by the processes not included in the model. Consider specifically $BaBiO_3$. U_{4+} in Table I is

$$U_{4+}=E(\mathrm{Bi}^{5+}{:}6s^0)+E(\mathrm{Bi}^{3+}{:}6s^2)-2E(\mathrm{Bi}^{4+}{:}6s^1)\,. \quad (2)$$

Each of the configurations is strongly charged; so one must consider nonlinear screening. The nonlinearity is such that the sum of the reduction in energy of the 5+ and the 3+ configurations will always be larger than twice the reduction in energy of the 4+ configuration. Suppose the screening of the $6s^2$ and the $6s$ configurations by charge transfer from the surrounding O^{2-} octahedra is not significant but the $6s^0$ (the most strongly charged) configuration is screened by charge transfer from the oxygen octahedra to the $6p$ shell. Now $E(6s^0 6p^1)-E(6s^0)\approx-43.3$ eV.[9] The electrostatic cost for one electron transfer is less than 12 eV. So even a fraction of electron transferred makes the effective U negative. There are other polarization processes included in the model we will discuss which also reduce U. The principal point is that, in the short-range effective interaction models for the s shell we shall consider, instability of a valence state requires $U<0$ for that state. The bare U for Bi^{4+} is already about 15 eV below the linear interpolation between that for Bi^{3+} and Bi^{5+}. Nonlinear screening and polarization do the rest.

In an "ionic" metal in which the conduction band has admixture of both anion and cation orbitals, it is essential to consider the effects of interatomic repulsion[10] besides the intra-atomic interactions. We therefore consider the model Hamiltonian

$$H=t\sum_{i,\delta,\sigma}c^{\dagger}_{ai\sigma}c_{bi+\delta\sigma}+U\sum_{i}n_{ai\sigma}n_{ai-\sigma}+V\sum_{i,\delta}n_{ai}n_{bi+\delta}-\Delta n_{bi\sigma}-\mu\sum_{i}(n_{ai}+n_{bi})\,. \quad (3)$$

a and b are the metal and oxygen atoms taken for simplicity to lie on a simple interpenetrating cubic lattice, δ sums over the nearest neighbors, and $U<0$, $V>0$.

To first order in $t/|\Delta|$, we may eliminate the b sites, obtaining an effective a-site Hamiltonian

$$\tilde{H}\simeq-\tilde{t}\sum_{i,\delta,\sigma}c^{\dagger}_{ai\sigma}c_{ai+2\delta\sigma}+\tilde{U}\sum_{i}n_{ai\sigma}n_{ai-\sigma}+\tilde{V}\sum_{i,\delta}n_{ai}n_{ai+2\delta}-\tilde{\mu}\sum_{i}n_{ai}\,. \quad (4)$$

Here $\tilde{t}=t^2/|\Delta|$, $\tilde{U}=U$, $\tilde{V}=zV|t/\Delta|^2$, $\tilde{\mu}=\mu$, and z is the number of nearest neighbors. To second order in V, polarization processes further reduce U; we do not consider them here. Actually for the compounds under discussion t/Δ is not a small parameter and the dynamical effects due to V are important.[10] They make the problem intractable analytically; we have not considered them here especially as $U<0$ has been assumed.

It is useful to transform (4) at arbitrary filling to a model with intrasite repulsion at half-filling by the transformation[11,12]

$$c_{ai\uparrow}\to c_{ai\uparrow};\quad c_{ai\downarrow}\to c^{\dagger}_{ai\downarrow}e^{i\mathbf{Q}\cdot\mathbf{R}_i},\quad Q\delta=\pi/2\,,$$

to get

$$\tilde{H}\simeq-\tilde{t}\sum_{i,\delta,\sigma}c^{\dagger}_{ai\sigma}c_{ai+2\delta\sigma}+|\tilde{U}|\sum_{i}n_{ai\uparrow}n_{ai\downarrow}+\tilde{V}\sum_{i,\delta}S^z_{ia}S^z_{i+2\delta a}+H\sum_{i}S^z_{ai}-|\tilde{U}|/2\sum_{i}n_{ai}\,, \quad (5)$$

where $H=\tilde{\mu}+|\tilde{U}|/2-2z\tilde{V}$. In the transformed Hamiltonian up spin at a site corresponds to a vacancy and a spin down to a doubly occupied site; the total magnetization $\sum_i\langle S^z_{ia}\rangle$ corresponds to deviations from half-filling in (4). Antiferromagnetic order with spins along the **z** direction (AFM-z) corresponds to a charge-density-wave phase while AFM order with spins in the x-y plane corresponds to s-wave superconductivity.

For $|\tilde{U}|\gg\tilde{t}$ (and $\gg\tilde{V}$), one may further transform (5) to an anisotropic Heisenberg model:

$$\mathbf{H}=\tilde{J}\sum_{i,\delta}\mathbf{S}_{ia}\cdot\mathbf{S}_{i+2\delta a}+\tilde{V}\sum_{i,\delta}S^z_{ia}S^z_{i+2\delta a}+H\sum_{i}S^z_{ia}\,, \quad (6)$$

$$\tilde{J}\approx2\tilde{t}^2/|\tilde{U}|\,.$$

The phase diagram for this model is well known[13] and experimentally well tested. For fixed H, the model has an AFM-z ground state from $H=0$ to $H=H_f=(2\tilde{V}\tilde{J}+\tilde{V}^2)^{1/2}$ where a first-order transition occurs to a phase which has AFM-xy order together with a magnetization in the z direction. The magnetization at the transition is $M_f\approx\chi_\perp H_f$, where $\chi_\perp\approx(\tilde{V}+\tilde{J})^{-1}$. At $H\approx\tilde{V}+\tilde{J}$, a transition to a fully magnetized phase occurs at $T\approx0$.

We must, however, consider the solution of (6) for fixed magnetization $\sum_i\langle S^z_{ai}\rangle$, i.e., fixed number in the original problem.[14] The model as it stands gives a two-phase coexistence region between $M=0$ and $M=M_f$. But this corresponds to droplets of a phase with one charge density in another. If longer-range (Coulomb or induced elastic) interactions are included in the model, the coexistence phase, as is usual, turns into a periodic array of discommensurations of one phase into another (or a superlattice of lines or points). The density of the discommensurations is given by the constraint on the magnetization, and their characteristic width is $\approx O((\tilde{J}/\tilde{H})^{1/2}\delta)$ for $\tilde{J}\gg\tilde{V}$ and $\approx\delta$ for $\tilde{V}\gg\tilde{J}$. We are clearly in the latter limit. The possibility of interfacial supercon-

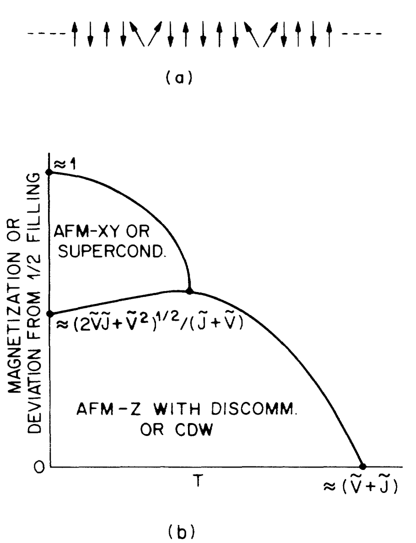

FIG. 1. (a) Schematic picture of the ground state of the anisotropic anitferromagnetic Heisenberg model at fixed magnetization for low magnetization. A down spin corresponds to a doubly occupied site, an up sign to a vacant site, and a tilted spin to a linear combination of the two in the original model. (b) Schematic phase diagram.

ductivity is then remote. The structure of this phase is schematically illustrated in Fig. 1(a).

At $H \approx (2\tilde{V}\tilde{J}+\tilde{V}^2)^{1/2}$, a phase transition occurs in the model to a phase which has AFM-xy order. The electronic density ϵ_0 corresponding to it is

$$\epsilon_0 \approx (2\tilde{V}\tilde{J}+\tilde{V}^2)^{1/2}/(\tilde{J}+\tilde{V}) . \tag{7}$$

We therefore have a superconducting phase near and above a deviation from half-filling ϵ_0. This phase would in general have short-range charge-density-wave order as well due especially to disorder.

We have considered the properties of the model in limits which may not be realistic. It is expected, however, that the generic behavior of the system is the same as given here—quantitative conclusions may vary. To be realistic we must also consider coupling to phonons.[15] Besides giving an additional negative contribution to U, they will distort the oxygen octahedra around different charge configurations of Bi by different amounts.

In this Letter we have presented evidence that about fifteen elements in the periodic table which skip valences in all their compounds do so because of a negative effective intra-atomic interaction at the skipped valence. At or near half-filling they are diamagnetic insulators, contrary to one-electron theory. They are also in a different class from Mott insulators. If they can be doped so that the average valence is considerably far from the skipped valence they turn to metals which are potential high-temperature superconductors. $BaPb_{1-x}Bi_xO_3$ and $Ba_xK_{1-x}BiO_3$ are realizations of this picture. Compounds formed of elements in Table I with the average valence between the skipped valence and the next higher valence should also be higher-temperature superconductors.

Our phase diagram [see Fig. 1(b)] agrees with that of $BaPb_{1-x}Bi_xO_3$ and $Ba_xK_{1-x}BiO_3$ in all essential respects[1-4] including the fact that the highest T_c is near the boundary with the insulating phase. The prediction of extra periodicity such as illustrated in Fig. 1(a) should be looked into. The fact that the gap in the optical spectra in the insulating phase persists as a pseudogap[16] in the superconducting phase is indication of a two-phase solution in the presence of disorder. Note that besides a negative U we have found it essential to include a near-neighbor repulsion parameter V to obtain the qualitatively correct phase diagram. We have emphasized elsewhere[10] that V is essential for superconductivity in the Cu-O based high-temperature superconductors as well.

I have benefitted from extensive discussions with Elihu Abrahams, B. I. Halperin, and Stefan Schmitt-Rink. D. R. Hamann kindly calculated the energy levels of Bi ions quoted above. Discussions with Bertram Batlogg and Robert Cava are also acknowledged.

---

[1] A. W. Sleight, J. J. Gillson, and P. E. Bierstedt, Solid State Commun. **17**, 27 (1975).

[2] D. E. Cox and A. W. Sleight, Acta Crystallogr. Sect. B **35**, 1 (1979); C. Chaillout, A. Santoro, J. P. Remeika, A. S. Cooper, G. P. Espinoza, and M. Marezio, Solid State Commun. **65**, 1363 (1988).

[3] T. D. Thanh, A. Koma, and S. Tanaka, Appl. Phys. **22**, 205 (1980).

[4] B. Batlogg, Physica (Amsterdam) **126B**, 275 (1984); B. Batlogg, J. P. Remeika, R. D. Dynes, H. Barz, A. S. Cooper, and J. P. Garno, in *Superconductivity in d- and f-band metals,* edited by W. Buckel and W. Weber (KFZ, Karlsruhe, 1982).

[5] R. J. Cava, B. Batlogg, J. J. Krajewski, R. Farow, L. W. Rupp, Jr., A. E. White, K. Short, W. F. Peck, and T. Kometani, Nature (London) **332**, 814 (1988); see also L. F. Mattheiss, E. M. Gyorgy, and D. W. Johnson, Jr., Phys. Rev. B **37**, 3745 (1985).

[6] P. W. Anderson, Phys. Rev. Lett. **34**, 953 (1975).

[7] *Handbook of Chemistry and Physics* (The Chemical Rubber Company, Cleveland, 1970-1971), 51st ed., p. E-74.

[8] C. Herring, *Magnetism,* edited by G. T. Rado and Harry Suhl (Academic, New York, 1966), Vol. IV, pp. 190-192.

[9] D. R. Hamann, private communication. These numbers are obtained from a density-functional calculation.

[10] C. M. Varma, S. Schmitt-Rink, and E. Abrahams, Solid State Commun. **62**, 681 (1987), and in *Novel Superconductivity,* edited by V. Kresin and S. Wolf (Plenum, New York, 1987).

[11] H. Shiba, Prog. Theor. Phys. **48**, 2171 (1972).

[12] S. Robaszkiewicz, R. Micnas, and K. A. Chao, Phys. Rev. B **23**, 1447 (1981), and **24**, 1579 (1981).

[13] See, for example, F. Keffer, *Handbuch der Physik,* edited by H. P. J. Wijn (Springer-Verlag, New York, 1966), Group 2,

Vol. XVIII.

[14] In Ref. 12 solutions to the model (4) and (6) were sought of the two-sublattice form. Then, instead of a charge-density-wave–only phase, a uniformly mixed charge-density-wave–superconducting phase is predicted. In such a solution the phase change across the discommensurations is spread uniformly over all the spins. Such a solution is in general unstable to the states proposed here.

[15] T. M. Rice and L. Sneddon, Phys. Rev. Lett. **47**, 689 (1981). W. Weber (private communication) calculates that electron-phonon interactions in the compounds under discussion lead to a T_c of less than 5 K. This is consistent with the isotope-shift measurements: B. Batlogg, R. J. Cava, and M. Stavola, Phys. Rev. Lett. **60**, 754 (1988).

[16] S. Uchida, S. Tajima, A. Masaki, S. Sugari, K. Kitazawa, and S. Tanaka, to be published.