

363 (1963) [Sov. At. Energy 15, 1105 (1963)].

³R. Goldberg and B. S. Liley, *Vacuum* 18, 631 (1968); B. S. Liley, C. F. Vance, and J. M. Smith, *Proc. Inst. Radio Electron. Eng.* 29, 221 (1968).

⁴D. L. Bowers, B. S. Liley, A. H. Morton, and C. F. Vance, to be published.

⁵A. A. Ware, *Phys. Rev. Lett.* 25, 15 (1970).

⁶A. A. Galeev and R. Z. Sagdeev, *Zh. Eksp. Teor. Fiz.* 53, 348 (1967) [Sov. Phys. JETP 26, 233 (1968)].

⁷P. H. Rutherford, *Phys. Fluids* 13, 482 (1970).

⁸T. E. Stringer, *Phys. Fluids* 13, 810 (1970).

⁹L. Spitzer, Jr., *Physics of Fully Ionized Gases*

(Interscience, New York, 1956), p. 77.

¹⁰H. P. Furth and M. N. Rosenbluth, in *Proceedings of the Third International Conference on Plasma Physics and Controlled Nuclear Fusion Research, Novosibirsk, U.S.S.R., 1968* (International Atomic Energy Agency, Vienna, Austria, 1969), Vol. 1, p. 821.

¹¹A. A. Ware and F. A. Haas, *Phys. Fluids* 9, 956 (1966).

¹²A. A. Ware, to be published.

¹³V. D. Shafranov, in *Reviews of Plasma Physics*, edited by M. A. Leontovich (Consultants Bureau, New York, 1967), Vol. 2, p. 127.

TIGHT BINDING AND TRANSITION-METAL SUPERCONDUCTIVITY*

S. Barišić,† J. Labbé, and J. Friedel

Laboratoire de Physique des Solides,‡ Faculté des Sciences de l'Université de Paris, 91 Orsay, France

(Received 6 July 1970)

The phonon-induced d - d coupling, calculated in tight-binding approximation, is shown to account for the order of magnitude of T_c in transition metals. The model relates the coupling constant to the cohesive energy rather than to the melting temperature as proposed by Matthias.

Recently it was suggested¹ that the superconductivity in transition metals is essentially due to phonon-induced d - p coupling. In the present work, we estimate the coupling term for a pure d band in tight-binding approximation and show that it can, alone, explain the order of magnitude of the superconducting transition temperature T_c , observed in transition metals and related alloys. This term is not incompatible with the general symmetry arguments presented in Ref. 1.

For the sake of simplicity, we choose to study a nondegenerate band of tightly bound electrons, described in the undeformed lattice (one atom per unit cell, six nearest neighbors) by the Hubbard Hamiltonian. When the lattice is deformed by displacing the ion on the site j from the position \vec{R}_j to $\vec{R}_j + \vec{u}_j$, we assume, as is usual in the study of one-dimensional systems^{2,3} and in some recent three-dimensional computations,⁴⁻⁶ that the tightly bound d function follows the displaced ion without notable deformation. For small displacements the quasiorthogonality relation of well-localized d functions remains valid. Therefore, we can introduce the operator a_j^\dagger creating the electron in the state $|d(\vec{r} - \vec{R}_j - \vec{u}_j)\rangle$, such that $(a_i^\dagger, a_j)_+ \approx \delta_{ij}$, and extend the Hubbard Hamiltonian to describe the deformed state:

$$H = \sum_{j,\alpha,\delta_\alpha,\sigma} J_{j,\delta_\alpha} a_{j,\sigma}^\dagger a_{j+\delta_\alpha,\sigma} + U \sum_j n_{j\uparrow} n_{j\downarrow}. \quad (1)$$

$J_{j,\delta_\alpha} = J(\vec{a}_{\delta_\alpha} + \vec{u}_{j+\delta_\alpha} - \vec{u}_j)$ is the overlap integral between the site j and one of two nearby sites δ_α lying on the lattice axis \vec{a}_α :

$$J(\vec{a}_{\delta_\alpha} + \vec{u}_{j+\delta_\alpha} - \vec{u}_j) = \int d(\vec{r} + \vec{a}_{\delta_\alpha} + \vec{u}_{j+\delta_\alpha} - \vec{u}_j) V(\vec{r}) d(\vec{r}) d^3\vec{r}. \quad (2)$$

Here $\vec{a}_{\delta_\alpha} = \vec{R}_{j+\delta_\alpha} - \vec{R}_j$ and $V(\vec{r})$ is the self-consistent potential attached to the site in the undeformed lattice and carried rigidly by the displaced ion. This is a supplementary approximation of our calculation. It is consistent with a rigid displacement of the d function if $\langle n_{j\sigma} \rangle$ does not change with respect to its value Q in undeformed state. It can be shown⁷ that even if one works with a long-range Hamiltonian instead of (1), but with an almost half-filled band, the self-consistency corrections arising from $\delta\langle n_{j\sigma} \rangle$ can be neglected with respect to the rigid-ion part of electron-phonon coupling constant. This latter is obtained on expanding the overlap integral (2) in the Hamiltonian (1) to the first order in $\vec{u}_{j+\delta_\alpha} - \vec{u}_j$:

$$J_{j\delta_\alpha} = J(\vec{a}_\alpha) + \left. \frac{\partial J(\vec{R})}{\partial \vec{R}} \right|_{\vec{R}=\vec{a}_{\delta_\alpha}} (\vec{u}_{j+\delta_\alpha} - \vec{u}_j). \quad (3)$$

Usually the symmetry of the d function with respect to the equilibrium lattice is such that the gradi-

ent of the overlap integral points along the lattice axis:

$$\left. \frac{\partial J(\vec{R})}{\partial \vec{R}} \right|_{\vec{a}_{\delta\alpha}} = -q_0 J(\vec{a}_\alpha) \frac{\vec{a}_{\delta\alpha}}{a_\alpha}$$

Here q_0 is the Slater coefficient describing the exponential, $e^{-q_0 r}$, decrease of the d function. It is usually of the order of 1 \AA^{-1} . If we expand \vec{u}_j in terms of phonon operators b_q and introduce the Fourier transform c_k of electron operators a_i , the linearized Hamiltonian (1) reads

$$H = \sum_{k\sigma} \epsilon_k c_{k\sigma}^\dagger c_{k\sigma} + \sum_{kq\sigma\nu} g_{kq}^\nu c_{k+q\sigma}^\dagger c_{k\sigma} (b_{q\nu} + b_{-q\nu}^\dagger) + \sum_j U n_{j\uparrow} n_{j\downarrow}, \quad (4)$$

where

$$\epsilon_k = \sum_\alpha 2J(\vec{a}_\alpha) \cos k_\alpha a_\alpha, \quad (5)$$

$$g_{kq}^\nu = \left(\frac{\hbar}{2NM\omega_{qv}^0} \right) I_{kk'}^\nu, \quad \vec{k}' = \vec{k} + \vec{q},$$

$$I_{kk'}^\nu = 2iq_0 \sum_\alpha J(\vec{a}_\alpha) \frac{\vec{a}_\alpha \cdot \vec{\epsilon}_q^\nu}{a_\alpha} (\sin k_\alpha a_\alpha - \sin k'_\alpha a_\alpha). \quad (6)$$

N is the number of atoms, M the ionic mass, ω_{qv}^0 the unrenormalized frequency of phonons of polarization $\vec{\epsilon}_q^\nu$. $I_{kk'}^\nu$ is the quantity appearing in McMillan's⁸ strong-coupling definition of the phonon-induced effective coupling constant λ ,

$$\lambda = \frac{n_F \langle I^2 \rangle}{M \langle \omega^2 \rangle} = \frac{n_F}{M \langle \omega^2 \rangle} \frac{\iint d\sigma d\sigma' \sum_\nu |I_{kk'}^\nu|^2 v_F^{-1} v_{F'}^{-1}}{\iint d\sigma d\sigma' v_F^{-1} v_{F'}^{-1}}. \quad (7)$$

$\langle \omega^2 \rangle$ is an appropriate average of the renormalized phonon frequency. n_F is the density of states per atom per spin at the Fermi level corresponding to the band energy (5), v_F the corresponding Fermi velocity, and $d\sigma$ and $d\sigma'$ are the elements of the Fermi surface corresponding to k and k' , respectively.

The coupling term (6) connects two neighboring Wigner-Seitz cells. Its order of magnitude—bandwidth/interatomic distance—agrees literally with the prediction of Ref. (8) based on a dimensional argument, which is in turn in agreement with experiments.

It was empirically observed^{8,11} that in superconducting transition metals the product $n_F \langle I^2 \rangle$ has a much smoother behavior than either of the two quantities n_F and $\langle I^2 \rangle$ separately. We examine now the possibility of such compensation in our simple model.

In what follows we restrict ourselves to the orthorhombic geometry with interatomic distances a_α not much different from one another. This still allows for a considerable anisotropy even for an s band since the small difference in a_α leads to appreciable differences in $J(\vec{a}_\alpha)$.

The sum over polarizations in Eq. (7) can be performed on using the fact that the polarization vectors form an orthonormal set. Therefore,

$$\sum_\nu [(\vec{a}_\alpha/a_\alpha) \cdot \vec{\epsilon}_q^\nu][(\vec{a}_\beta/a_\beta) \cdot \vec{\epsilon}_q^\nu] = \delta_{\alpha\beta}$$

and hence

$$\sum_\nu |I_{kk'}^\nu|^2 = 4q_0^2 \sum_\alpha J^2(\vec{a}_\alpha) (\sin k_\alpha a_\alpha - \sin k'_\alpha a_\alpha)^2.$$

Introducing the electron velocity $v_k^\alpha = \hbar^{-1} \partial \epsilon_k / \partial k_\alpha$ and noting that the cross term in the squared bracket vanishes by symmetry it follows that

$$\langle I^2 \rangle \simeq 2\hbar^2 q_0^2 a^{-2} \langle v_F^2 \rangle \quad (8)$$

with

$$\langle v_F^2 \rangle = \int v_F d\sigma / \int v_F^{-1} d\sigma.$$

The integral in the denominator of Eq. (8) cancels with the density of states in the product⁹ $n_F \langle I^2 \rangle$, while the remaining integration over the Fermi surface can be transformed by Gauss's theorem into an integration within the enclosed volume of the reciprocal space. In this way, we find

$$\begin{aligned} n_F \langle I^2 \rangle &\simeq q_0^2 E_c, \\ E_c &= -2 \int^{E_F} \epsilon n(\epsilon) d\epsilon. \end{aligned} \quad (9)$$

The energy ϵ is measured here from the middle of the band. E_c represents the direct contribution of tightly bound electrons to the cohesive energy of the crystal. This quantity was extensively studied by Cyrot-Lackman¹⁰ for different models of the density of states. As a result, E_c has a quite regular, paraboliclike, behavior as a function of band occupation Q and is always con-

vex with respect to the Q axis, whatever the density of states is. For a not too asymmetric density of states, E_c passes through a broad maximum in the vicinity of a half-filled band. Hence, in the region where $n_F \langle I^2 \rangle$ is strongest, so that it can overcome the Coulomb repulsion, it is also weakly dependent on Q .

Formulation (8) is established in the simple, one-band, six-neighbors model but is, perhaps, more general than the model itself. With suitable behavior of $\langle \omega^2 \rangle$ this would also agree with the suggestion¹¹ of Matthias that the lower the melting point the weaker the superconductivity of the transition metal. Actually, Eq. (8) relates T_c to the cohesive energy rather than to the melting point. But these two quantities scale¹² much in the same way in these elements. At the present stage of understanding of transition metal superconductivity it is thus interesting to compare the values of $n_F \langle I^2 \rangle$ obtained from the measured¹² cohesive energy and Eq. (8) on one hand and from empirical values of λ and $\langle \omega^2 \rangle$ on the other hand.

In the latter case $\langle \omega^2 \rangle$ was determined from neutron experiments⁸ for V, Nb, Ta, Mo, and W, since the Debye Θ_D does not provide a sufficiently reliable estimate of the average phonon frequency. The values¹ of $n_F \langle I^2 \rangle$ for Ti, Zr, Hf, and Re are less accurate since the neutron work is not yet available for these elements.

The only remaining parameter, q_0 , in our Eq. (8) is determined by fitting the McMillan $n_F \langle I^2 \rangle$ for V and Ta, and assumed constant throughout the corresponding period. For the fifth ($4d$) period, q_0 is obtained by interpolation. The three (reasonable) values for q_0 are thus 0.93, 0.91, and 0.87 \AA^{-1} for fourth, fifth, and sixth period, respectively. The numerical results are listed in Table I.

We note that the relative smallness¹³ of $n_F \langle I^2 \rangle$ in the fourth period is accounted for by Eq. (8) without playing on q_0^2 values. Equation (8) accounts also for the approximate constancy of $n_F \langle I^2 \rangle$ in the middle of each period but predicts a smoother decrease of $n_F \langle I^2 \rangle$ in the fourth group than observed, and does not account for the small secondary peak at Re. This can be due either to the crudeness of our computation or to the inaccuracy of $n_F \langle I^2 \rangle$ values obtained with $\langle \omega^2 \rangle$ estimated from specific heat data. Finally, the values of $q_0^2 E_c$ for Cr, Mn, and Fe in Table I are predicted by interpolation between V and Co, because the measured cohesive energy in these metals probably contains an important exchange contribution, not appearing in E_c defined by Eq. (8).

Table I. Numerical results. E_c is the measured value of the cohesive energy; $q_0^2 E_c$ is obtained on multiplying this value by q_0^2 except for Cr, Mn, and Fe. Values given for $n_F \langle I^2 \rangle$ are as estimated by Hopfield (H) or McMillan (M). The starred elements are superconducting.

$q_0 = 0.93 \text{ \AA}^{-1}$	Ti *	V *	Cr	Mn	Fe	Co
E_c (ev/at)	4.85	5.3	4.1	2.9	4.3	4.4
$q_0^2 E_c$ (ev/ \AA^2 at)	4.2	(4.6)	≈ 4.8	≈ 4.6	≈ 4.2	3.8
$n_F \langle I^2 \rangle$ (ev/ \AA^2 at)	2.7 ^H	4.6 ^M				
$q_0 = 0.91 \text{ \AA}^{-1}$	Zr *	Nb *	Mo *	Tc *	Ru *	Rh
E_c (ev/at)	6.3	7.6	6.8	6.6	6.7	5.8
$q_0^2 E_c$ (ev/ \AA^2 at)	5.2	6.3	5.7	5.5	5.6	4.8
$n_F \langle I^2 \rangle$ (ev/ \AA^2 at)	3.0 ^H	7.2 ^M	6.8 ^M			
$q_0 = 0.87 \text{ \AA}^{-1}$	Hf *	Ta *	W *	Re *	Os *	Ir *
E_c (ev/at)	6.3	8.1	8.6	8.1	8.1	6.9
$q_0^2 E_c$ (ev/ \AA^2 at)	4.8	(6.1)	6.5	6.1	6.1	5.2
$n_F \langle I^2 \rangle$ (ev/ \AA^2 at)	2.7 ^H	6.1 ^M	6.3 ^M	8.1 ^H		

In conclusion, the present calculation accounts for the order of magnitude of T_c in transition metals on the basis of the intraband d - d coupling alone.¹⁴ The good numerical agreement obtained for transition metals should be confirmed by computations using more realistic structure of the d band than that used in the present model.

*The work presented here is a portion of a Ph.D. thesis which will be submitted by S. B. to the Faculté des Sciences d'Orsay.

†On temporal leave from the Institute of Physics, University of Zagreb, Zagreb, Yugoslavia.

‡Associé au Centre National de la Recherche Scientifique.

¹J. J. Hopfield, Phys. Rev. **186**, 443 (1969).

²R. A. Harris and L. M. Falicov, *J. Chem. Phys.* **51**, 5034 (1969) and references therein.

³C. Tric, *J. Polym. Sci. C* **29**, 119 (1970).

⁴J. Labbé, *J. Phys.* **29**, 195 (1968).

⁵H. Fröhlich and T. K. Mitra, *J. Phys. C: Proc. Phys. Soc., London* **1**, 548 (1968).

⁶T. K. Mitra, *J. Phys. C: Proc. Phys. Soc., London* **2**, 52 (1969).

⁷S. Barišić, thesis, to be published.

⁸W. L. McMillan, *Phys. Rev.* **167**, 331 (1968).

⁹The complete elimination of the density of states depends, however, on the averaging procedure, Eq. (7), adopted by McMillan. For an alternative definition see D. J. Scalapino, in *Superconductivity*, edited by R. D. Parks (Marcel Dekker, New York, 1969), Chap. 10, III A. With his definition, $\langle v_F^2 \rangle$ in Eq. (8) must be replaced by $\frac{1}{2}\langle v_F^2 \rangle$ where $\langle v_F^2 \rangle = \int v_F^2 d\sigma / \int d\sigma$. The two ex-

pressions for $\langle I^2 \rangle$ may differ appreciably only close to a sharp peak in the density of states. For the BCS treatment of the latter case see J. Labbé, S. Barišić, and J. Friedel, *Phys. Rev. Lett.* **19**, 1039 (1967).

¹⁰F. Cyrot-Lackmann, *J. Phys. Chem. Solids* **29**, 1235 (1968).

¹¹B. T. Matthias, *First Advanced Summer Study on Superconductivity, McGill University, 1968* (Gordon and Breach, New York, 1969).

¹²K. A. Gschneidner, *Solid State Phys.* **16**, 275 (1964).

¹³See also K. Andres, E. Bucher, J. P. Maita, and R. C. Sherwood, *Phys. Rev.* **178**, 702 (1969).

¹⁴The empirical arguments in favor of such a point of view are reviewed by G. Gladstone, M. A. Jensen, and J. R. Schrieffer, in *Superconductivity*, edited by R. D. Parks (Marcel Dekker, New York, 1969), Chap. 13, V D.

TWO-PHOTON MAGNETOABSORPTION IN ZnO†

R. Dinges, D. Fröhlich, B. Staginnus, and W. Staude

Physikalisches Institut der Universität Frankfurt am Main, Frankfurt am Main, Germany

(Received 20 July 1970)

Two-photon magnetoabsorption experiments are reported for the first time. From the splitting of the $2p$ excitons of ZnO in a magnetic field of 42 kG the hole masses and the g values for the upper valence bands Γ_9 and Γ_7 are deduced.

Two-photon spectroscopy has gained growing importance as a spectroscopic method in studying electronic properties in solids. Because of the changed selection rules as compared with ordinary spectroscopy (one-photon absorption), two-photon data yield information on excited states which are commonly forbidden for one-photon transitions.¹ Two-photon measurements with polarized light allow symmetry assignments to be determined for the different excited states. Much more quantitative information on band parameters (e.g., effective masses, g values) are expected from two-photon magnetoabsorption, since transitions with $\Delta m = \pm 2$, ± 1 , and 0 are two-photon allowed, as compared with $\Delta m = \pm 1$ and 0 in one-photon absorption. In this Letter we report the first observation of two-photon magneto-optic absorption in ZnO. Because of its rather large band gap (3.5 eV) and its pronounced exciton structure, ZnO is well suited for this kind of experiment. One-photon data^{2,3} on ZnO show three well-resolved exciton series, which are interpreted as transitions to S excitons from the three valence bands [symmetry Γ_7 (A), Γ_9 (B), and Γ_7 (C)] and a Γ_7 conduction band. The two-photon spectrum looks quite different: It shows very narrow exciton lines close to the

corresponding $2s$ transitions. This is shown for the A and B excitons in Fig. 1. For polarization parallel to the c axis one gets in one-photon absorption the C series and in two-photon absorption again a single pronounced exciton line,⁴ which is close to the $2s$ line in the one-photon spectrum. We interpret the two-photon lines as transitions to $2p$ excitons. The shift of about 2.5 meV to lower energies as compared with the

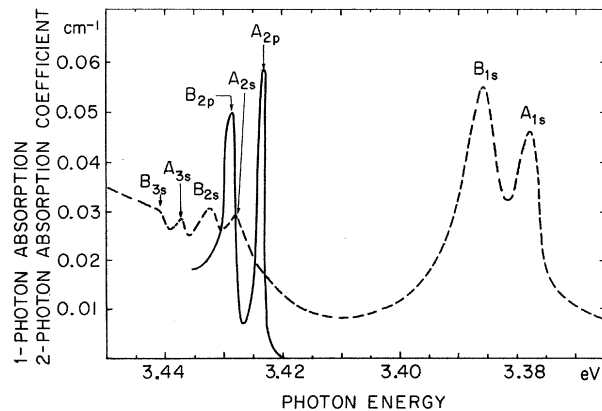


FIG. 1. Dashed line, one-photon spectrum (Ref. 3) of ZnO at 4.2°K, polarization $\perp c$ axis. Solid line, two-photon spectrum of ZnO at 1.6°K, polarization $\perp c$ axis. Laser flux: 10^{26} photons/cm² sec.