

#### IV. CONCLUSIONS

By taking account of exchange interactions between itinerant  $d$  electrons by means of an effective exchange field, we have found a magnetic diffusion coefficient  $D = (v^2/3\omega_0)\{\omega_0\tau/[1+(\omega_0\tau)^2]\}$  which approaches the usual independent-particle form for small translational relaxation time  $\tau$ , but instead of increasing monotonically with  $\tau$  goes through a maximum and returns to zero. We also find a  $\tau$ -dependent contribution to the exchange stiffness. The effect of these terms will be small, especially at low temperatures.

Obviously, independent  $d$  electrons plus an effective-field type of spin-spin correlation does not tell the whole

story in a ferromagnetic metal, but we think it plausible that the real situation can be well described by a Fermi-liquid picture with spin splitting, with a varying axis of spin quantization corresponding to the varying direction of the macroscopic magnetization. Such a model would have transport properties similar to those of the present simplified model.

#### ACKNOWLEDGMENTS

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### Remark on the Hopping Transition Probability of Polaron Holes in NiO

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For the hopping motion of polaron holes the frequency factor  $W_0$  of the transition probability is determined by the observation that hole localization occurs in a molecular orbital of the irreducible set  $t_{2g}$  of a cation site group (with transfer integral  $b_\pi$ ), whereas the superexchange mechanism is caused by virtual charge transfers between molecular orbitals of the irreducible set  $e_g$  (with transfer integral  $b_\sigma$ ). The effect of short-range magnetic ordering on  $W_0$  is determined by the time-dependent spin-pair correlation function  $\gamma_{ij}(t)$  for neighbor cations  $i$  and  $j$  and for times  $t \gg t_0$  = relaxation time for the correlation.

#### I. INTRODUCTION

FOR nonmagnetic ionic crystals the theory of small polaron conduction has been developed by Yamashita and Kurosawa,<sup>1</sup> Holstein,<sup>2</sup> and Sewell.<sup>3</sup> If one wants to apply the results to a concrete case and calculate the dc conductivity of  $p$ -type material, one has four unknown parameters, namely, the acceptor concentration  $N_p$  and the activation energy  $E_p$  determining the concentration of mobile holes, the hopping activation energy  $E_0$ , and the frequency factor of the transition probability  $W_0$ . A theoretical discussion of  $W_0$  is the object of this note. For bound holes hopping around acceptor sites, it can be determined from the frequency and temperature dependence of the ac conductivity or of the internal friction.<sup>4,5</sup> For mobile holes traveling through the lattice, an unambiguous experimental determination of  $W_0$  is difficult, as can be

seen from the attempt of Y and K to determine it from Morin's<sup>6</sup> experimental data on conductivity and Seebeck coefficient. The magnitude of  $W_0$ , however, is of some interest because it can be quite different for the two types of hopping transitions: Adiabatic over-the-barrier transitions for which  $W_0 = \omega_0/2\pi$  ( $\omega_0$  = frequency of longitudinal optical vibration), and non-adiabatic through-the-barrier tunneling transitions for which  $W_0$  is determined by a transfer integral between ligand field orbitals. Therefore, we wish to discuss here:

- (1) The relative magnitude of  $W_0$  for the two types of transitions;
- (2) the effect of magnetic ordering on  $W_0$ .

The first point has received the attention of Y and K and of Herring<sup>7</sup>; the authors come to opposite conclusions. The second point has been considered by Heikes.<sup>8</sup> His result, that  $W_0$  calculated by Y and K and by H is multiplied by a factor depending on the sublattice magnetization  $\mathbf{M}$  characterizing long-range order of the

<sup>1</sup> J. Yamashita and T. Kurosawa, *J. Phys. Chem. Solids* **5**, 34 (1958); *J. Phys. Soc. Japan* **15**, 802 (1960); referred to as Y and K.

<sup>2</sup> T. Holstein, *Ann. Phys.* **8**, 325, 343 (1959); referred to as H.

<sup>3</sup> G. L. Sewell, *Phys. Rev.* **129**, 597 (1962).

<sup>4</sup> D. P. Snowden and H. Saltsburg, *Phys. Rev. Letters* **14**, 497 (1965).

<sup>5</sup> S. Van Houten, *J. Phys. Chem. Solids* **23**, 1045 (1962); S. Van Houten and A. J. Bosman, in *Transition Metal Compounds*, edited by E. R. Schatz (Gordon and Breach Science Publishers, Inc., New York, 1964), p. 123.

<sup>6</sup> F. J. Morin, *Phys. Rev.* **93**, 1199 (1953).

<sup>7</sup> C. Herring, *Proceedings of the International Conference on Semiconductor Physics*, Prague, 1960, p. 60.

<sup>8</sup> R. Heikes, in *Transition Metal Compounds*, edited by E. R. Schatz (Gordon and Breach Science Publishers, Inc., New York, 1964), p. 1.

spin system, appears at first sight surprising because it is the short-range correlation between ionic spins which governs the spin transfer accompanying a hopping transition. We shall find, with a proper discussion of the time-dependent spin-pair correlation function, that Heikes' result is essentially correct.

The basic assumption for the following discussion is that at temperatures  $T \gtrsim \theta_0/2$ , where  $\theta_0 = \hbar\omega_0/k$ , a single hole in an otherwise perfect NiO crystal is localized in a molecular orbital of a nickel ion.<sup>9</sup> The binding energy  $E_b \approx E_d - J$ , where  $E_d$  is the deformation energy gained when a single hole is introduced at a Ni<sup>++</sup> site and the lattice is allowed to relax and where  $J$  is the relevant transfer integral which determines the width of the hole band for the rigid lattice. From an estimate of  $E_d$  by Y and K ( $\approx 2.4$  eV) and by Van Houten<sup>10</sup> ( $\approx 1.8$  eV) and from the value of  $J$  ( $\approx 0.35$  eV) known from the superexchange energy, the assumption of hole localization appears well justified.<sup>11</sup>

## II. NONADIABATIC AND ADIABATIC TRANSITIONS

Transitions between localized states centered at neighbor nickel ions can occur because of a finite coherence of the hole wave functions centered at the two sites and because thermal excitations of the lattice provide the energy necessary to overcome the potential barrier. At high temperatures  $T > \theta_0$ , the results of Y and K and of H for the transition probability  $W$  are in exact agreement and are given by<sup>12</sup>

$$W = W_0 e^{-E_0/kT}, \quad (1)$$

where the hopping activation energy  $E_0 < E_b$ . The frequency factor is given by

$$W_0 = \begin{cases} (\pi/4kTE_0)^{1/2} J^2/\hbar, & \text{nonadiabatic transitions} \\ \omega_0/2\pi, & \text{adiabatic transitions.} \end{cases} \quad (2)$$

The transfer integral  $J$  is the matrix element of the perturbing potential (consisting of the ionic potential of the perfect lattice minus the potential of the initial ion) between hole wave functions centered at neighbor nickel ions. Nonadiabatic transitions are predominant if  $J \ll \hbar\omega_0$ . Then, the elementary transition probability corresponds to a process in which a hole absorbs and/or emits a number of phonons, thereby arriving at energy

resonance with an unoccupied polaron hole state centered at a neighbor ion, so that it can tunnel through the potential barrier. The thermal average of these processes gives  $W$  (non-ad). Its exponential dependence on the strength of the interaction between hole and lattice arises from overlap integrals of oscillator wave functions for the initial and for the final polaron state.<sup>13</sup> On the other hand, if the coherence is sufficiently large,  $J \gg \hbar\omega_0$ , the hole follows adiabatically a "favorable" thermal fluctuation of the potential and travels over the barrier to a neighbor site. The transfer integral must, however, not be too large ( $J \ll E_d$ ); otherwise, polaron band conduction occurs.<sup>14</sup>

In comparing Morin's experimental results for the dc conductivity of Li<sub>0.1</sub>Ni<sub>0.9</sub>O with their theory, Y and K find that at high temperatures the hopping transitions are nonadiabatic. On the other hand, Herring<sup>7</sup> suggests that the adiabatic approximation should in general work fairly well for transition metal oxides. Herring's argument is based on the magnitude of the transfer integral  $b_\sigma$  which enters as a crucial parameter Anderson's theory of the antiferromagnetic state. The question then arises: Is the  $b_\sigma$  relevant for Anderson's<sup>15</sup> expression of the superexchange energy also the appropriate transfer integral for hopping transitions in NiO?

The answer depends on the ground-state configuration of the  $3d^7$  complex, i.e., Ni<sup>2+</sup> ion plus hole, in an otherwise perfect NiO crystal. Assuming that the crystalline field surrounding the  $3d^7$  complex is described with a point-ion model, we have the following alternatives<sup>16</sup>: first, 5 electrons occupy states of the irreducible set  $t_{2g}$  of the ion site group (= cubic point group), with symmetry like  $xy$ ,  $yz$ ,  $zx$ , and 2 electrons occupy states of the irreducible set  $e_g$ , with symmetry like  $2z^2 - x^2 - y^2$ ,  $y^2 - x^2$ ; second, the alternate configuration has 6 electrons in  $t_{2g}$  states and 1 electron in an  $e_g$  state. Which configuration is actually occupied depends primarily on the relative magnitude of two energies, the crystal field splitting  $\Delta = 10Dq$  between  $e_g$  and  $t_{2g}$  states, and the mean pairing energy  $\Pi$ <sup>17</sup> of  $d$  electrons in the  $e_g$  set. For a free ion, this energy enforces Hund's rule. If the latter overrides the crystal field energy (see Fig. 1),

$$\Delta < \Pi, \quad (\text{high-spin complex})$$

the hole "occupies" a  $t_{2g}$  state. In the opposite case,

$$\Delta > \Pi, \quad (\text{low-spin complex})$$

it occupies an  $e_g$  state. At this point, where we shall

<sup>9</sup> R. R. Heikes and W. D. Johnston, J. Chem. Phys. **26**, 582 (1957), first suggested polaron hole localization at cation sites.

<sup>10</sup> S. Van Houten, J. Phys. Chem. Solids **17**, 7 (1960).

<sup>11</sup> Since Y and K employ the zeroth-order approximation of N. F. Mott and M. J. Littleton, Trans. Faraday Soc. **34**, 485 (1938), they overestimate  $E_d$ . In this approximation  $E_d$  depends on  $1 - 1/\epsilon_0$ , where  $\epsilon_0$  is the static dielectric constant; however, the continuum approximation for  $\epsilon_0$  breaks down in the vicinity of the excess charge. Van Houten (Ref. 10) employs the first-order approximation of Mott and Littleton and finds a more reliable value for  $E_d$ .

<sup>12</sup> At high temperatures, the "diagonal" transitions, which Y and K have not subtracted from their total transition probability, are unimportant.

<sup>13</sup> K. Huang and A. Rhys, Proc. Roy. Soc. (London) **A204**, 406 (1951).

<sup>14</sup> At present there is no theory which allows for a "smooth transition" between hopping and band conduction. Holstein (see Ref. 2) points out, however, that this transition is rather sharp.

<sup>15</sup> P. W. Anderson, Phys. Rev. **115**, 2 (1959).

<sup>16</sup> H. A. Bethe, Ann. Physik **3**, 133 (1929).

<sup>17</sup> J. S. Griffith and L. E. Orgel, Quarterly Rev. (London) **11**, 381 (1957).

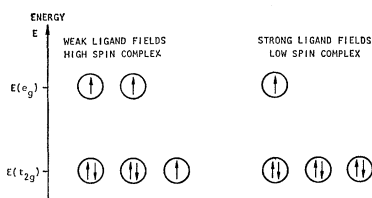


FIG. 1. Spin arrangement for the  $e_g$  and  $t_{2g}$  orbitals in weak and strong octahedral ligand fields. For strong fields the ground-state energy of the  $3d^7$  complex is given by  $6E(t_{2g}) + 1E(e_g)$ , whereas for weak fields the corresponding energy is  $5E(t_{2g}) + 2E(e_g) - \Pi$ , where  $\Pi$  is the pairing energy enforcing Hund's rule.

compare the best available semiempirical values of  $\Delta$  and  $\Pi$ , it must be mentioned that atomic  $3d$  functions, or proper linear combinations, cannot be considered as accurate one-electron wave functions. In particular, the orthogonality required between accurate one-electron wave functions of the real crystal leads to a covalent admixture of ligand wave functions into the irreducible sets of atomic  $3d$  orbitals (see Figs. 2 and 3).<sup>18</sup> It is assumed that the resulting molecular orbitals exist as accurate one-electron wave functions of the magnetic ions and that the energies  $\Delta$  and  $\Pi$  refer to these states. From the observed optical absorption spectrum of a NiO single crystal, Newman and Chrenko<sup>19</sup> find that the crystal field parameter ( $Dq$ ) for  $O^{2-}$  octahedra is  $910 \text{ cm}^{-1}$ . Assuming that

$$Dq_{Ni^{3+}} = 2Dq_{Ni^{2+}} \quad (3)$$

as in the comparable case of Co,<sup>20</sup> we have

$$\Delta_{Ni^{3+}} \approx 18\,000 \text{ cm}^{-1}.$$

This value is probably an upper limit; for most of the other  $3d$  transition metal ions  $Dq_{M^{3+}}/Dq_{M^{2+}} < 2$ . The mean pairing energy  $\Pi$  for ions of the first transition metal series, surrounded by octahedra of water molecules, has been calculated independently by Griffith<sup>21</sup> and by Orgel.<sup>22</sup> Both find approximately the same results.<sup>17</sup> Since  $\Pi$  is not very sensitive to the nature of

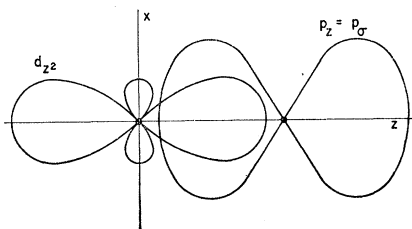


FIG. 2. Symmetry relation between  $d_{z^2}$  and  $p_\sigma$  orbital.

<sup>18</sup> J. H. Van Vleck, *J. Chem. Phys.* **3**, 803, 807 (1935).

<sup>19</sup> R. Newman and R. M. Chrenko, *Phys. Rev.* **114**, 1507 (1959).

<sup>20</sup> P. W. Anderson, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1963), Vol. 14, p. 184.

<sup>21</sup> J. S. Griffith, *J. Inorg. Nucl. Chem.* **2**, 1, 229 (1956).

<sup>22</sup> L. E. Orgel, *J. Chem. Phys.* **23**, 1819 (1955).

the ligands, we can take their value for the trivalent ion,

$$\Pi_{Ni^{3+}} \approx 27\,000 \text{ cm}^{-1},$$

to find that the  $3d^7$  complex is in the high spin configuration (see Fig. 1).<sup>23</sup> A reasonable estimate for the effect of spin-orbit coupling, the most important correction to  $\Delta$  and  $\Pi$ ,<sup>24</sup> is given by the spin-orbit splitting of the triplet  $F$  state of the  $Ni^{2+}$  ion. It amounts to  $1360 \text{ cm}^{-1}$ , which is small compared with  $(\Pi - \Delta)_{Ni^{3+}}$ ,<sup>25</sup>

Now we come to the transfer integral  $J$  of Eq. (2) and its magnitude. Since the polaron hole occupies a  $t_{2g}$  orbital,  $J$  is not identical with the transfer integral  $b_\sigma$  which plays a central role in Anderson's mechanism of superexchange;  $b_\sigma$  is the transfer integral between two  $e_g$  orbitals centered around magnetic ions diametrically opposite a ligand ion ( $Ni^{2+} - O^{2-} - Ni^{2+}$ ). The relevant  $e_g$  orbital is of the form (see Fig. 2)<sup>26</sup>

$$\psi_{e_g} = C_{e_g}(d_{z^2} - \lambda_\sigma p_\sigma - \lambda_s s), \quad (4)$$

where  $C_{e_g}$  is a normalization constant,  $d_{z^2}$  is a linear combination of atomic  $d$  orbitals with symmetry like

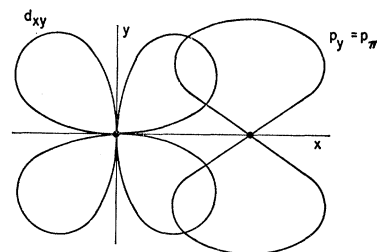


FIG. 3. Symmetry relation between  $d_{xy}$  and  $p_\pi$  orbital.

$2z^2 - x^2 - y^2$ ;  $p_\sigma$  is the  $2p$  part of the anion wave function directed toward the origin of the cation,  $s$  denotes the anion  $2s$  function, and the  $\lambda$ 's are covalency parameters. On the other hand, the polaron hole occupies a  $t_{2g}$  orbital which is of the form

$$\psi_{t_{2g}} = C_{t_{2g}}(d_{xy} - \lambda_\pi p_\pi), \quad (5)$$

where  $d_{xy}$  has the symmetry of  $xy$  and  $p_\pi$  is a linear combination of two  $2p$  orbitals transforming like  $x$  and  $y$  (see Fig. 3). A polaron hole in a  $t_{2g}$  orbital has the two transfer integrals. The first connects to a nearest-neighbor cation with parallel spin. This transfer integral is determined by the overlap of  $d_{xy}$  functions centered at these cations. The distance between neighbor cations is  $a/\sqrt{2} = 2.97 \text{ \AA}$ , where the cubic lattice constant  $a = 4.196 \text{ \AA}$  for NiO.<sup>27</sup> The empirical  $Ni^{2+}$  radius is

<sup>23</sup> This confirms an earlier suggestion by Van Houten (Ref. 10); however, here the discussion is based on a more accurate value for the ratio  $\Delta_{Ni^{3+}}/\Delta_{Ni^{2+}}$ .

<sup>24</sup> J. Kanamori, *Progr. Theoret. Phys. (Kyoto)* **17**, 177 (1957).

<sup>25</sup> Also, the displacement polarization will affect  $\Delta$  which depends on overlap and covalency parameters (see Ref. 19); however, the net change in  $\Delta$  is probably small compared with  $(\Pi - \Delta)_{Ni^{3+}}$ .

<sup>26</sup> See R. G. Shulman and S. Sugano, *Phys. Rev.* **130**, 506 (1963).

<sup>27</sup> H. P. Rooksby, *Acta Cryst.* **1**, 286 (1948).

0.7 Å, and the Ni<sup>2+</sup> radius is 0.6 Å.<sup>28</sup> Therefore, the direct overlap of  $d_{xy}$  orbitals is small; Switendick<sup>29</sup> finds that the transfer integral between two  $d_{xy}$  orbitals, centered around neighbor cations in the  $xy$  plane and denoted as  $(d\pi d\pi)$  by Slater and Koster,<sup>30</sup> is 0.108 eV. The transfer integral between two corresponding  $\psi_{t_{2g}}$  orbitals is considerably smaller than  $(d\pi d\pi)$  and depends on the covalency parameter  $\lambda_\pi$  in Eq. (5). On the other hand, there is appreciable overlap between such  $\psi_{t_{2g}}$  orbitals because the lobes of the  $d_{xy}$  functions, though they do not point directly toward the intermediate anion, overlap via the  $p_\pi$  function of the ligand ion (see Fig. 3). The value of  $b_\pi$  is not accurately known at present; it depends on  $\lambda_\pi$  and, furthermore, on the matrix element between the  $d_{xy}$  and the  $p_y$  orbital of neighbor ions defined as  $(pd\pi)$  by Slater and Koster.<sup>30</sup> Anderson<sup>15</sup> estimates  $b_\pi = \frac{1}{3}b_\sigma$ , where the transfer integral  $b_\sigma$  relevant for the superexchange mechanism is known, from the experimental value of the Néel temperature, to be of the magnitude 0.35 eV, so that  $b_\pi \approx 0.12$  eV. This value of  $b_\pi$  cannot be far from the true value since Switendick<sup>29</sup> finds for NiO that  $(pd\pi)/(pd\sigma) \approx 0.4$ . Therefore, we may assume that  $b_\pi$  is only a small fraction of  $b_\sigma$  (one-third) and is of comparable magnitude with  $\hbar\omega_0 = 0.076$  eV. Since the transfer integral is neither small nor large compared with  $\hbar\omega_0$ , let us compare numerical values of Eq. (2) for the two different types of transitions. From Eq. (2) it is seen that adiabatic transitions are dominant if

$$b_\pi \gg E_0^{1/4} (2kT/\pi)^{1/4} (\hbar\omega_0/\pi)^{1/2}. \quad (6)$$

The exact value of  $E_0$  is not known, but the right side of Eq. (6) depends only on its quartic root. With the reasonable assumption  $5 \lesssim E_0/\hbar\omega_0 \lesssim 10$ , Eq. (6) is fulfilled if  $b_\pi \gg \frac{2}{3}\hbar\omega_0$ . We have seen that this is not the case;  $b_\pi/\hbar\omega_0$  is perhaps 1 to 3 and, therefore,  $W_0(\text{non-ad}) \approx \omega_0/2\pi$ . To summarize: If one ignores magnetic ordering, adiabatic and nonadiabatic hopping transitions between  $t_{2g}$  orbitals centered opposite a ligand ion are of equal importance for the polaron hole charge transfer,  $W_0 \approx \omega_0/2\pi$ .

### III. EFFECT OF SHORT-RANGE MAGNETIC ORDER ON $W_0$

A hopping transition between neighbor cations  $i$  and  $j$  is accompanied by a spin transfer, and since the perturbation causing the transitions is spin-independent, the charge carrier does not change its spin during the transition. Then, the transition probability is reduced by a factor

$$\Omega_{ij} = \frac{1}{2} (1 + \bar{\gamma}_{ij}/s_i s_j), \quad (7)$$

<sup>28</sup> R. E. Watson and A. J. Freeman, Phys. Rev. **120**, 1125 (1960), have calculated  $d$  electron densities of Ni<sup>2+</sup> ions surrounded by an octahedral array of point charges, with a Hartree-Fock self-consistent-field calculation.

<sup>29</sup> A. C. Switendick, Solid State and Molecular Theory Group, MIT, Quarterly Progress Report **49**, 41 (1963) (unpublished).

<sup>30</sup> J. C. Slater and G. F. Koster, Phys. Rev. **94**, 1498 (1954).

where  $\bar{\gamma}_{ij}$  is the mean value [Eq. (9)] of the time-dependent spin-pair correlation function

$$\gamma_{ij}(t) = \langle \mathbf{s}_i(0) \cdot \mathbf{s}_j(t) \rangle_T, \quad (8)$$

defined by van Hove,<sup>31</sup> for a spin system described by the Heisenberg interaction between ionic spins  $\mathbf{s}_i$  and  $\mathbf{s}_j$ . The bracket  $\langle \rangle_T$  refers to the mean value over a canonical distribution at temperature  $T$ . If two cations  $i$  and  $j$ , opposite a ligand ion, have opposite spin, then  $\Omega_{ij} = 0$ . In general, the ionic spins are not antiparallel because of: (a) a local distortion of the ground-state spin arrangement caused by the additional spin of a charge carrier at site  $i$ ; and (b) thermal fluctuations of ionic spin directions. The local spin distortion caused by a hole at site  $i$  can be calculated with the help of de Gennes'<sup>32</sup> theory. Then, it is seen that this distortion, as well as its effect on the polaron binding energy, is negligible because the transfer integral  $b_\pi$  is so small that the gain of binding energy due to spin canting in the vicinity of site  $i$  plus the simultaneous increase in superexchange energy is minimized by distortion angles of only a few degrees. Therefore, at temperatures  $T \gtrsim \frac{1}{2}\theta_0$ , where hole localization occurs, it is the thermal fluctuation of the relative orientation of the ionic spins  $\mathbf{s}_i$  and  $\mathbf{s}_j$  which determines  $\Omega$ . The relevant spin-pair correlation function  $\gamma_{ij}(t)$  is proportional to  $\cos\theta_{ij}$ , where  $\theta_{ij}$  is the angle between  $\mathbf{s}_i(0)$  and  $\mathbf{s}_j(t)$ . It is assumed that this function remains unaffected by the presence of the hole. The hole sits initially at site  $i$ , where it spends on the average a time  $\tau$ , that is, the mean time-of-stay. During this time the spin orientations fluctuate and a proper mean value of the relative orientation of  $\mathbf{s}_i$  and  $\mathbf{s}_j$  can be defined as

$$\bar{\gamma}_{ij} = \frac{1}{\tau} \int_0^\tau \gamma_{ij}(t) dt. \quad (9)$$

The time dependence of the spin-pair correlation function  $\gamma_{ij}(t)$  is not exactly known. A fair estimate  $\bar{\gamma}_{ij}$  is found by taking into account that the relaxation time of the correlation (8) is much smaller than the mean time which a hole spends at a cation site,  $t_0 \ll \tau$ . For a time  $t \gg t_0$ , the two ionic spins  $\mathbf{s}_i(0)$  and  $\mathbf{s}_j(t)$  are statistically independent, that is, the correlation is given by

$$\gamma_{ij}(t) = \langle \mathbf{s}_i \rangle_T \cdot \langle \mathbf{s}_j \rangle_T, \quad \text{for } t \gg t_0, \quad (10)$$

where  $\langle \mathbf{s}_i \rangle_T$  is the average spin vector per ion at temperature  $T$ . Above the Néel temperature  $T_N$ ,  $\langle \mathbf{s}_i \rangle_T = 0$ ; below  $T_N$  one has  $\langle \mathbf{s}_i \rangle_T = \mathbf{M}(T)$ , the magnetization of a sublattice. Since the hopping transitions occur between cations belonging to sublattices with opposite spin (at  $T = 0^\circ\text{K}$ ), one has, with Eqs. (7) and (10),

$$\Omega = \frac{1}{2} [1 - \mathbf{M}^2(T)/\mathbf{M}^2(0)]. \quad (11)$$

<sup>31</sup> A. van Hove, Phys. Rev. **95**, 1374 (1954).

<sup>32</sup> P. G. de Gennes, Phys. Rev. **118**, 141 (1960).

This expression is somewhat different from that of Heikes, who first suggested that  $\Omega$  depends only on  $\mathbf{M}(T)$ . This is correct provided the pertinent assumption  $t_0 \ll \tau$  is fulfilled. Now, the relaxation time  $t_0$  is of the order of  $\hbar/J_{\text{eff}}$ .<sup>31</sup> Here  $J_{\text{eff}} = b_\pi^2/U$ , where  $U$  measures the Coulomb repulsion between two electrons at the same ion. From Van Vleck's relation between  $T_N = 520^\circ\text{K}$  and  $J_{\text{eff}}$ , one finds  $(J_{\text{eff}})_{\text{exp}} = 0.022$  eV and  $t_0 \sim 3 \times 10^{-14}$  sec. On the other hand, it follows from Eq. (2) that the mean time-of-stay  $\tau = 1/W \ll \hbar\omega_0$ , so that in fact  $t_0 \ll \tau$ .

#### IV. CONCLUSION

Mobile polaron holes in NiO are localized in molecular orbitals of  $t_{2g}$  symmetry, corresponding to the high spin configuration of the trivalent cation. The transfer integral  $b_\pi$  between two  $t_{2g}$  orbitals centered opposite a ligand ion determines the coherence between polaron hole wave functions and is the pertinent parameter for real hopping transitions of polaron holes. The value of  $b_\pi$  is only  $\sim \frac{1}{3}$  of the transfer integral  $b_\sigma$  connecting orbitals of  $e_g$ -symmetry between which virtual transitions of electrons take place, causing the superexchange mechanism proposed by Anderson. Since  $b_\pi$  is of the

same magnitude as the phonon energy  $\hbar\omega_0$ , the frequency factor for nonadiabatic through-the-barrier tunneling transitions is of comparable magnitude with that for adiabatic over-the-barrier transitions; therefore, if one ignores magnetic ordering,  $W_0 \approx \omega_0/2\pi$ . The effect of magnetic ordering on the transition probability  $W$  is determined by the time-dependent spin-pair correlation function  $\gamma_{ij}(t)$  for two neighbor cations  $i$  and  $j$  of different sublattices. Since the mean time-of-stay  $\tau = 1/W \gg t_0$  (= the relaxation time for the correlation  $\gamma_{ij}$ ), the pair correlation is given by the time-independent expression of  $\gamma_{ij}(t \gg t_0)$ . This merely depends on the sublattice magnetization  $\mathbf{M}(T)$ , and the effect of magnetic ordering is accounted for with

$$W_0 \approx \Omega\omega_0/2\pi = (\omega_0/4\pi)[1 - \mathbf{M}^2(T)/\mathbf{M}^2(0)]. \quad (12)$$

At  $T = 300^\circ\text{K}$ , the effect of magnetic ordering leads to  $\Omega = \frac{1}{10}$ .

#### ACKNOWLEDGMENTS

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### Magnetic Structures of Field-Cooled and Stress-Cooled Chromium\*

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Single crystals of chromium have been cooled through the Néel temperature in an applied magnetic field of 55 kG (field cooling) and with an applied compressive stress of 0.7 kg mm<sup>-2</sup> (stress cooling). The resulting magnetic structures of both states have been determined, by neutron diffraction, at temperatures of 78 and 294°K. The results are consistent with the assumption that field cooling favors the nucleation and growth of domains in which there exists a spin-density wave (SDW) with its vector parallel to the direction of the field applied during cooling; in stress cooling the development of domains with a SDW vector parallel to the direction of compressive stress is inhibited. Data on the anisotropy of magnetic susceptibility of field-cooled chromium suggest that the susceptibility of a SDW is maximum when measured normal to the direction of spin polarization. Data on the effect of field cooling on the anomalous temperature dependence of the resistivity of chromium near the Néel temperature are also discussed.

#### I. INTRODUCTION

NEUTRON-diffraction investigations<sup>1-5</sup> have shown that high-purity chromium exists in two

antiferromagnetic phases which, following Hamaguchi *et al.*,<sup>6</sup> are referred to below as the AF<sub>1</sub> and AF<sub>2</sub> phases. The AF<sub>1</sub> phase is stable in the range from the Néel temperature  $T_N = 311$  to about 120°K; the AF<sub>2</sub> phase is stable at temperatures below 120°K. The phase transformation from AF<sub>1</sub> to AF<sub>2</sub> has been characterized as a change in the direction of antiferromagnetism and the temperature at which the transformation occurs is known as the spin-flip temperature  $T_{sf}$ . Overhauser<sup>7</sup> has reviewed the evidence which indicates that the

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