

Orbital Order and Ferrimagnetic Properties of $\text{Sr}_8\text{CaRe}_3\text{Cu}_4\text{O}_{24}$

Xiangang Wan,^{1,2} Masanori Kohno,¹ and Xiao Hu¹

¹Computational Materials Science Center, National Institute for Materials Science, Tsukuba 305-0047, Japan

²National Laboratory of Solid State Microstructures and Department of Physics, Nanjing University, Nanjing 210093, China

(Received 24 May 2004; published 3 March 2005)

By means of the LSDA + U (local spin density approximation plus Hubbard U) method and the Green function method, we investigate the electronic and magnetic properties of the new material of $\text{Sr}_8\text{CaRe}_3\text{Cu}_4\text{O}_{24}$. Our LSDA + U calculation shows that this system is an insulator of ferrimagnetism with a net magnetic moment of $1.01\mu_B/\text{f.u.}$, which is in good agreement with the experiment. It is the nonmagnetic Re atoms that induce an orbital order of d electrons of Cu atoms, which is responsible for the strong exchange interaction and the high magnetic transition temperature. Based on the LSDA + U results, we introduce an effective model for the spin degrees of freedom and investigate the finite-temperature properties by the Green function method. The obtained results are consistent with the experimental results, indicating that the spin-alternating Heisenberg model is suitable for this compound.

DOI: 10.1103/PhysRevLett.94.087205

PACS numbers: 75.10.Jm, 71.70.Gm, 75.30.Et

Perovskite transition-metal oxides have been investigated intensively [1]. The discoveries of high- T_c superconductivity [2] and colossal magnetoresistance (CMR) [3] in this family of materials pose a significant challenge to the theoretical understanding of the strongly correlated electron systems.

In certain parameter regimes, strong Coulomb repulsions make electrons localized and the materials behave as Mott insulators. In this phase, low-energy excitations are dominated by the superexchange interaction [4], and the collective excitations of spin degrees of freedom govern the physics. The parent materials of high- T_c superconductors (HTSC) are such typical examples. Their properties are well described by a spin-1/2 antiferromagnetic (AFM) Heisenberg model on a square lattice. It is widely believed that properties of the parent systems are closely related to the origin of high- T_c superconductivity [5].

It is also well known that the charge distribution in perovskite transition-metal oxides is influenced strongly by the crystal field, i.e., the degeneracy of the $3d$ electrons is lifted by lattice distortions of the perovskite structure in various ways. Therefore, the spin, charge, and orbital degrees of freedom intertwine with each other, which make the physics of the perovskite transition-metal oxides very rich. These features are shared by materials in which CMR are observed [6].

As revealed in this Letter, the recently synthesized material $\text{Sr}_8\text{CaRe}_3\text{Cu}_4\text{O}_{24}$, which forms the perovskite structure as shown in Fig. 1(a), is another member of this family of materials [7]. The new material is similar to the parent materials of HTSC in the following aspects: (i) perovskite structure, (ii) magnetic insulator, and (iii) Cu surrounded by O. However, it is different in the points that this material is three dimensional (3D) and has nonzero magnetization in the ground state $M \approx 0.95\mu_B$ per formula unit (f.u.). Also, this compound is peculiar since ferromagnetic (FM) cuprates are very rare, and it has an unusually high mag-

netic transition temperature $T_c \approx 440$ K. Curie temperatures T_c of known FM cuprates are usually quite low. For example, the T_c of $\text{La}_4\text{BaCu}_2\text{O}_{10}$, K_2CuF_4 , and SeCuO_3 are 5, 6.5, and 26 K, respectively [8]. Therefore, it is interesting to see why a strong magnetic state is realized in this material. Although the response of the compound to carrier doping is also very interesting, we concentrate here on the undoped material. It is shown that both the electron-electron correlation and the coupling between orbital and spin degrees of freedom are important for this compound, which results in a 3D spin-alternative Heisenberg Hamiltonian.

We calculate the electronic and magnetic structures of $\text{Sr}_8\text{CaRe}_3\text{Cu}_4\text{O}_{24}$ by using the WIEN2K package [9], which is an implementation of the density-functional augmented-plane wave + local orbitals method [10]. The muffin-tin sphere radii of 2.0, 2.0, 2.0, 1.9, and 1.5 a.u. are chosen for the Ca, Cu, Sr, Re, and O atoms, respectively, with $RK_{\text{max}} = 7.0$, which results in about 5200 linear augmented-plane waves and local orbitals per cell. We use 700 k points in the Brillouin zone. As for the exchange-correlation potential, we adopt the standard generalized gradient approximation (GGA) [11] and use the experimental structure in the calculation [12]. The GGA calculation predicts this material as a metal inconsistent

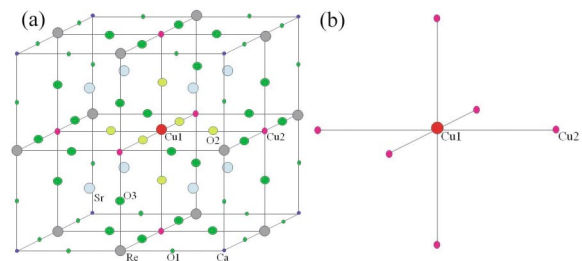


FIG. 1 (color). Crystal structure of $\text{Sr}_8\text{CaRe}_3\text{Cu}_4\text{O}_{24}$. (a) Unit cell. (b) Unit cell of the effective model.

TABLE I. Calculated total energy E_{tot} relative to the energy of FiM configuration in units of Ry, the total magnetic moments per unit cell μ_{tot} , and the magnetic moment inside the muffin-tin sphere of Cu1, Cu2, and O2 in units of μ_B .

	E_{tot}	μ_{tot}	Cu1	Cu2	O2
FM	0.036	5.01	1.15	0.84	0.14
FiM	0	-1.01	1.09	-0.81	0.07

with the experiment, which indicates that the electron-electron interactions are important for this compound. Thus, we use the LSDA + U (local spin density approximation plus Hubbard U) method [13] to take them into account, and we adopt $U = 10$ eV and $J = 1.20$ eV for the d orbital of Cu [14].

In order to investigate the magnetic structures and interactions of $\text{Sr}_3\text{CaRe}_3\text{Cu}_4\text{O}_{24}$, we calculate both ferrimagnetic (FiM) and FM configurations for Cu1 and Cu2 moments. The results are shown in Table I. Magnetic moments are mainly located at Cu1 and Cu2 sites in both configurations with the magnitude almost independent of the configuration. The magnetic moments at Ca, Sr, O1, and O3 are smaller than $0.001\mu_B$. Thus, they are negligible compared to the moments at Cu. O2 carries a small but nonvanishing moment due to large hybridization with Cu1 and Cu2. Our numerical results show that the FiM state is the ground state with net magnetic moment $M = 1.01\mu_B/\text{f.u.}$ This is quantitatively consistent with the experimental one. Also, the ground state is an insulator with the energy gap of 1.68 eV consistent with the experimental result [7]. It should be noted that the magnetic moment at the Re atom is very small (less than $0.004\mu_B$) in both configurations. This feature is contrasted with the ordered double perovskite $A_2\text{FeMO}_6$, where due to the hybridization with d orbitals of Fe, the nonmagnetic ion M possesses a large magnetic moment and plays a significant role in the magnetic properties [15,16]. We also performed calculations for $U = 8$ and 12 eV to cover a wide range of generally accepted values of correlations. Numerical results show that the magnetic moments are not sensitive to U . With decreasing U , the energy difference between FiM and FM (ΔE) increases slightly. For example, the calculated ΔE for $U = 8$ eV is higher than that of $U = 10$ eV by about 20%.

Figure 2(a) shows the calculated charge density plotted in the (010) plane of Fig. 1(a). The charge density along the Re-O3 bonds is significantly larger than that along Cu2-O3, and the Re-O3 bond is shorter than that of Cu2-O3. Therefore, there is a Jahn-Teller distortion in the oxygen octahedron centered at Cu2 consisting of four O3 and two O2 atoms with the bond length of Cu2-O2 smaller than that of Cu2-O3. Consequently, the e_g orbital of Cu2 splits into $d_{3z^2-r^2}$ and $d_{x^2-y^2}$. The former, which points to O2, has a higher energy than the latter. Thus, as shown in Fig. 3(b), the partially occupied orbital in Cu2 is the minority spin

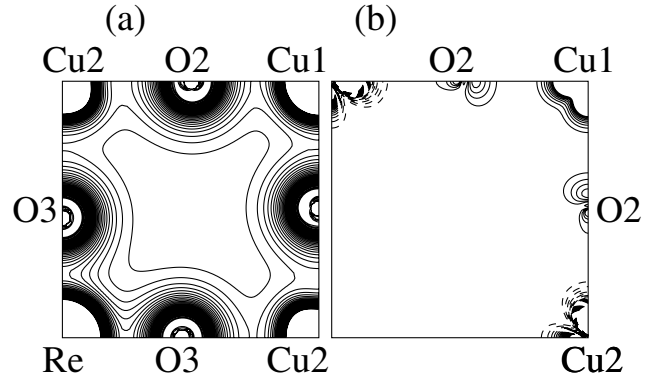


FIG. 2. Contours for charge density in the (010) plane with interval $0.03e/\text{bohr}^3$. (a) Total charge density. (b) Spin density (spin-up charge density minus spin-down charge density). The dotted lines are negative contours.

(spin up) $d_{3z^2-r^2}$ (all the other d orbitals of Cu2 are fully occupied). In contrast, three crystallographic directions of Cu1 are completely equivalent, and the oxygen octahedron centered at the Cu1 site is free of any distortion. Therefore, different from Cu2, the e_g and t_{2g} orbitals of Cu1 are still fully degenerate, respectively, and all d orbitals except for the e_g orbital of minority spin (spin down) are fully occupied as shown in Fig. 3(a). In addition, the $2p$ states of O2 distribute mainly in the energy range from -7.0 to 0.0 eV and are almost fully occupied.

The spin density shown in Fig. 2(b) clearly indicates that the magnetic moments of the Cu1 and Cu2 are carried mostly by e_g and $d_{3z^2-r^2}$ orbitals, respectively. In Fig. 4,

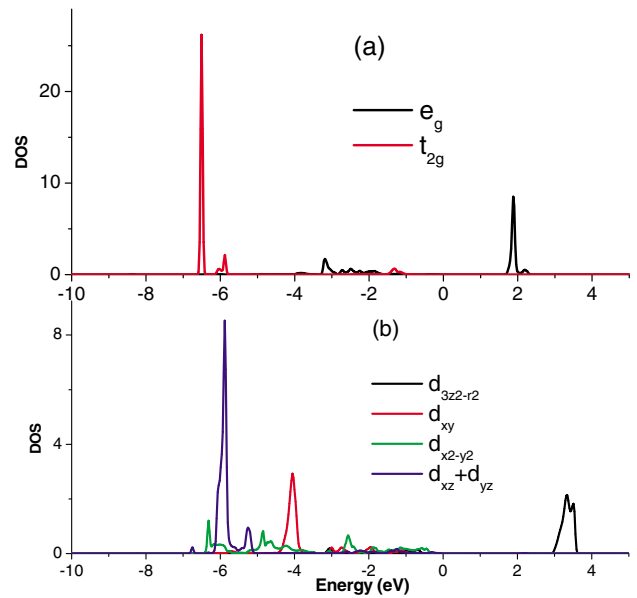


FIG. 3 (color). Projected density of state with Fermi energy at zero. (a) For minority spin (spin down) d orbital of Cu1. (b) For minority spin (spin up) d orbital of Cu2.

we schematically show the partially occupied d orbitals of Cu1 and Cu2 and the almost fully occupied p_z orbital of O2 for the material. It is interesting to observe that an orbital ordering appears at Cu sites. The minority spin $d_{3z^2-r^2}$ orbital of Cu2 and the e_g orbital of Cu1 are pointing to the O2 as shown in Fig. 4. Both of them are almost empty. Meanwhile, the almost fully occupied p_z orbital of O2 points to the neighboring Cu1 and Cu2 sites. Therefore, the spin-up and spin-down p_z orbitals of O2 strongly overlap with the spin-up $d_{3z^2-r^2}$ orbital of Cu2 and the spin-down e_g orbital of Cu1, respectively, to form a rather strong $pd\sigma$ hybridization. This results in a strong exchange interaction between the magnetic moments at Cu1 and Cu2 and a high transition temperature.

In order to further clarify the effects of Re, we perform a calculation for an artificial structure where the Jahn-Teller distortion in the oxygen octahedron centered at Cu2 is removed. We find that the orbital ordering still survives, and the results are very similar to that of the real structure. We then change Re to technetium, which is the element at the same column in the periodic table. Our calculation shows that the partially occupied orbital of Cu2 changes from $d_{3z^2-r^2}$ to $d_{x^2-y^2}$, which is orthogonal to the orbitals of O2. Consequently, the spin interaction becomes much weaker. As a result, the energy difference between FiM and FM configurations is reduced greatly. Therefore, the Re atoms play an important role for the orbital ordering to cause the unusually high T_c , although their magnetic moments are very small.

Since the magnetic moments are almost localized at Cu sites, the effective model for the spin degrees of freedom of this material is expected to be a Heisenberg model, where neighboring localized spins at Cu sites interact antiferro-

magnetically. Although the simple ionic model ($\text{Cu}^{2+}\text{-O}^{2-}$ or $\text{Cu}^{3+}\text{-O}^{2-}$) is not exact due to the large hybridization between Cu and O, we still take spins at Cu sites as a good quantum number similar to the case of the parent materials of HTSC. We consider the following two cases: (i) $S_1 = 1$, $S_2 = 1/2$ and (ii) $S_1 = S_2 = 1/2$, where S_i denotes the spin length at the Cu i site. The magnetization in the unit cell for the FiM state and that of the FM state are obtained as (i) $M_{\text{FiM}} = 1\mu_B$, $M_{\text{FM}} = 5\mu_B$ and (ii) $M_{\text{FiM}} = 2\mu_B$, $M_{\text{FM}} = 4\mu_B$, noting that the g factor is 2. The LSDA + U result is $M_{\text{FiM}} = 1.01\mu_B$, $M_{\text{FM}} = 5.01\mu_B$ as shown in Table I. Hence, case (i) is reasonable. Thus, the effective Hamiltonian becomes

$$\mathcal{H} = J_{\text{eff}} \sum_i \mathbf{S}_i \cdot \sum_p \mathbf{s}_{i+(p/2)}, \quad (1)$$

where J_{eff} is the effective exchange interaction, i runs over Cu1 sites, and p denotes the unit vectors of the unit cell in the lattice shown in Fig. 1(b) ($p = \pm\hat{x}, \pm\hat{y}, \pm\hat{z}$). Here, \mathbf{S}_i and $\mathbf{s}_{i+(p/2)}$ denote the spin operator of $S = 1$ at the Cu1 site (i) and that of $S = 1/2$ at the Cu2 site ($i + \frac{p}{2}$), respectively.

Since this model is on a bipartite lattice and belongs to the family in which the Marshall-Lieb-Mattis theorem holds [17], the ground state of this model is proven to have spin $S = 1/2 (= 1/2 \times 3 - 1)$ in any size system. This results in spontaneous magnetization $M = 1\mu_B$ in the bulk limit and well explains the experimental result ($M \approx 0.95\mu_B$) [7].

Since the difference of the magnitude of magnetic moments at Cu sites between FM and FiM states is small as shown in Table I, the energy difference between FM and FiM, $\Delta E = 0.036 \text{ Ry} = 5679 \text{ K}$, can be assigned to the exchange interaction. By diagonalizing the Hamiltonian (1) in the unit cell, we evaluate the energy difference between FM and FiM configuration as $8J_{\text{eff}}$. Hence, we estimate $J_{\text{eff}} = \Delta E/8 = 710 \text{ K}$. In order to take quantum fluctuations into account, we apply the Green function method [18] which is a standard approach to investigate the temperature dependence of magnetism. We construct 16 Green functions of Cu1 spins and Cu2 spins and obtain closed coupled equations for Green functions by using Tyablikov's decoupling [19], assuming that the fluctuations around $\langle s^z \rangle$ and $\langle S^z \rangle$ are small. Following Callen's scheme [20], we obtain $\langle s^z \rangle$ and $\langle S^z \rangle$ as a function of spin-wave dispersion relations E_k . Here, E_k is also a function of $\langle s^z \rangle$ and $\langle S^z \rangle$. Thus, we solve these coupled equations numerically to obtain $\langle s^z \rangle$ and $\langle S^z \rangle$ at finite temperatures.

The result of the Green function method for the spontaneous magnetization is shown in Fig. 5. In the low-temperature limit, spontaneous magnetization M obtained by the Green function method is about $1\mu_B$, which is consistent with the exact result $M = 1\mu_B$ and the experimental result $M \approx 0.95\mu_B$. Magnetic transition temperature T_c is calculated as $T_c = 448 \text{ K}$ by the Green function

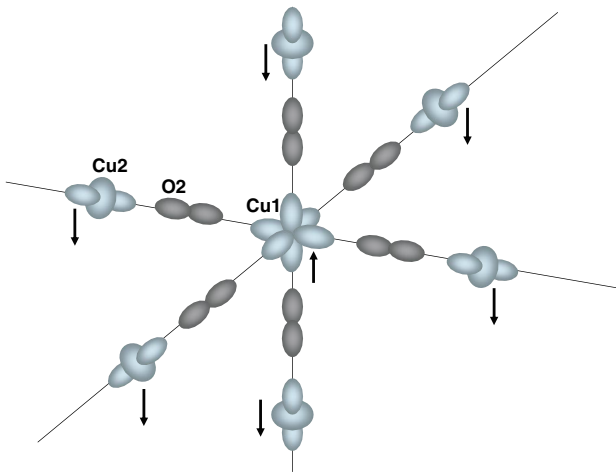


FIG. 4 (color). Schematic picture for the spin and orbital orders of $\text{Sr}_8\text{CaRe}_3\text{Cu}_4\text{O}_{24}$ deduced from the LSDA + U calculation. The gray symbols denote the partially occupied d orbital, and the dark ones denote the fully occupied p orbital. The arrows denote the directions of magnetic moments on Cu sites.

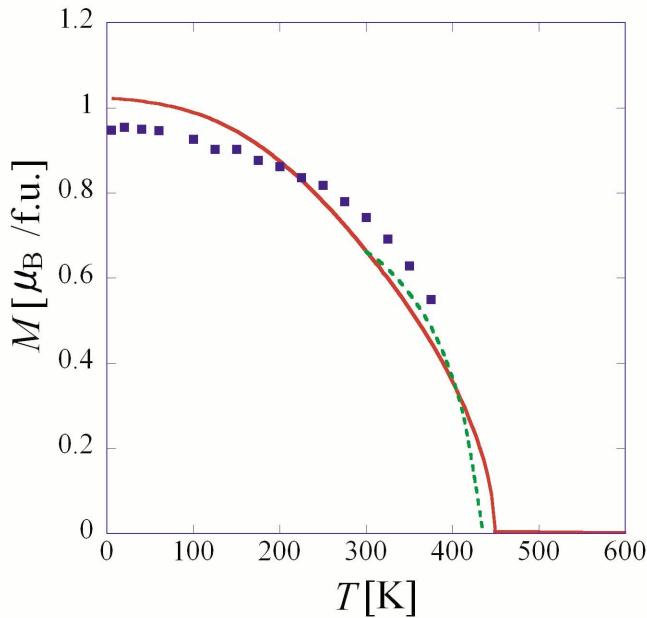


FIG. 5 (color). Temperature dependence of the spontaneous magnetization. The solid curve denotes the result of the Green function method. Squares and the dotted line are experimental results in Ref. [7].

method, which is close to the experimental result $T_c \simeq 440$ K. Thus, the magnetic properties known so far in $\text{Sr}_8\text{CaRe}_3\text{Cu}_4\text{O}_{24}$ are explained by the spin-alternating Heisenberg model defined in Eq. (1).

Here, we summarize the mechanism of ferrimagnetism and the high magnetic transition temperature T_c for $\text{Sr}_8\text{CaRe}_3\text{Cu}_4\text{O}_{24}$. The mechanism of the AFM coupling is the superexchange [4]. The large exchange constant J_{eff} is due to the large overlap between Cu and O2 orbitals and to the localization of Cu spins by strong correlations. This situation is similar to the case of the parent materials of HTSC. In contrast to them, the number of sublattice sites is different. This causes ferrimagnetism. Imbalance of the spin length between Cu1 and Cu2 sites would also be a reason for stabilization of the ferrimagnetic state.

In summary, using the LSDA + U method, we have investigated the electronic and magnetic properties of $\text{Sr}_8\text{CaRe}_3\text{Cu}_4\text{O}_{24}$. Our results are in good agreement with the experimental results and show that the nonmagnetic transition-metal Re plays an important role in determining the magnetic properties of this material. Namely, Re induces orbital orderings of the d orbitals in Cu. This results in the strong exchange coupling between the magnetic moments of Cu and the unusually high T_c . Based on the LSDA + U results, we have introduced a 3D spin-alternating Heisenberg model and investigated the magnetic properties by the Green function method. The obtained temperature dependence of the spontaneous magnetization and T_c are consistent with the experimental ones. Since one-dimensional spin-alternating systems ex-

hibit peculiar magnetic properties, it is expected that the 3D spin-alternating Heisenberg system can also show interesting physical properties. Both theoretical and experimental investigations are highly anticipated.

We acknowledge Dr. E. Takayama-Muromachi for bringing our attention to this material and for valuable discussions. Dr. M. Arai and Dr. M. Katakiri are appreciated for their technical help. This work was partially supported by Japan Society for the Promotion of Science [Grant-in-Aid for Scientific Research (C) No. 15540355].

-
- [1] See, for example, M. Imada, A. Fujimori, and Y. Tokura, *Rev. Mod. Phys.* **70**, 1039 (1998).
 - [2] J. G. Bednorz and K. A. Müller, *Z. Phys. B* **64**, 189 (1986).
 - [3] S. Jin *et al.*, *Science* **264**, 413 (1994); P. Schiffer *et al.*, *Phys. Rev. Lett.* **75**, 3336 (1995).
 - [4] H. A. Kramers, *Physica (Utrecht)* **1**, 182 (1934); P. W. Anderson, *Phys. Rev.* **115**, 2 (1959).
 - [5] F. C. Zhang and T. M. Rice, *Phys. Rev. B* **37**, 3759 (1988).
 - [6] C. N. R. Cao *et al.*, *J. Phys. Condens. Matter* **12**, R83 (2000); M. B. Salamon and M. Jaime, *Rev. Mod. Phys.* **73**, 583 (2001).
 - [7] E. Takayama-Muromachi *et al.*, *J. Solid State Chem.* **175**, 366 (2003).
 - [8] F. Mizuno *et al.*, *Nature (London)* **345**, 788 (1990); I. Yamada, *J. Phys. Soc. Jpn.* **33**, 979 (1972); K. Kohn *et al.*, *J. Solid State Chem.* **18**, 27 (1976).
 - [9] P. Blaha *et al.*, *WIEN2K, An Augmented Plane Wave + Local Orbitals Program for Calculating Crystal Properties*, edited by K. Schwarz (TU Wien, Wien, Austria, 2001), ISBN 3-9501031-1-2.
 - [10] E. Sjöstedt, L. Nordström, and D. J. Singh, *Solid State Commun.* **114**, 15 (2000); G. K. H. Madsen *et al.*, *Phys. Rev. B* **64**, 195134 (2001).
 - [11] J. P. Perdew, K. Burke, and M. Ernzerhof, *Phys. Rev. Lett.* **77**, 3865 (1996).
 - [12] We have performed the structural optimization and find that the difference between the theoretical and experimental structures is very small. The optimization has a very small effect on the electronic and magnetic properties of this compound. Therefore, we present only results based on the experimentally reported structural parameters.
 - [13] V. I. Anisimov, J. Zaanen, and O. K. Andersen, *Phys. Rev. B* **44**, 943 (1991); V. I. Anisimov *et al.*, *Phys. Rev. B* **48**, 16929 (1993); M. T. Czyzyk, and G. A. Sawatzky, *Phys. Rev. B* **49**, 14211 (1994).
 - [14] V. I. Anisimov *et al.*, *Phys. Rev. B* **66**, 100502 (2002).
 - [15] D. D. Sarma *et al.*, *Phys. Rev. Lett.* **85**, 2549 (2000).
 - [16] Z. Fang, K. Terakura, and J. Kanamori, *Phys. Rev. B* **63**, 180407 (2001); J. Kanamori and K. Terakura, *J. Phys. Soc. Jpn.* **70**, 1433 (2001).
 - [17] W. Marshall, *Proc. R. Soc. London A* **232**, 48 (1955); E. Lieb and D. Mattis, *J. Math. Phys. (N.Y.)* **3**, 749 (1962).
 - [18] N. N. Bogolyubov and S. V. Tyablikov, *Dokl. Akad. Nauk SSSR* **126**, 53 (1959) [*Sov. Phys. Dokl.* **4**, 589 (1959)].
 - [19] S. V. Tyablikov, *Ukr. Mat. Zh.* **11**, 287 (1959).
 - [20] H. B. Callen, *Phys. Rev.* **130**, 890 (1963).