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Multiple-Band Conduction in *n*-Type Rutile (TiO_2)†

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The existence of multiple-band conduction in *n*-type rutile for temperatures above ≈40°K is deduced from studies of the Hall coefficients and electrical conductivities from ≈2 to 600°K. This investigation emphasizes the anisotropy of the Hall coefficients, i.e., the Hall effect measured with magnetic fields along the *a* and the *c* axis, respectively (R_a and R_c). The pronounced temperature dependence of the ratio of these two coefficients can most easily be interpreted on the basis of two competing conduction processes. Measurements on samples with widely differing charge-carrier concentrations prove that the conduction processes involved are due to intrinsic energy states of the crystal. The energy separation between the lowest conduction band and the bottom of the next higher one is calculated to be 0.05 (estimated error: ±0.01 eV). These concepts are consistent with recent band-structure calculations. Impurity and surface conduction are shown to be negligible.

I. INTRODUCTION

RUTILE is a semiconducting oxide for which conduction in conventional broad bands has been amply demonstrated. This aspect and other electronic properties have been extensively reviewed.[1–5]

Recent studies of the Hall coefficient and electrical conductivity on *n*-type material have suggested that multiple-band conduction[6] and complex scattering processes[7] occur near room temperature. A theoretical estimate of the energy band structure[8] supports these concepts.

The present article includes more complete data and analysis to test the hypothesis of multiple band conduction as well as to check possible competing effects such as impurity or surface conduction.

II. EXPERIMENTAL PROCEDURES

The sources of single crystals, their purity, preparation of samples, and measurement techniques have been described previously[2,6]; however, more recent innovations include: (1) reduction of ≈10-×10-×3-mm single-crystal prisms and subsequent cutting into narrower, oriented samples for measurement. The direction of the primary current is always chosen along the largest dimension of the samples (*l* direction). This results in more nearly identical samples ("pairs") with the desired orientations and amount of doping than we have been able to obtain by first cutting the specimens and then reducing them simultaneously in the same system.[2,6] (2) Vacuums obtained by a Vac-Ion pump ($\sim 2\times 10^{-7}$ Torr) demonstrate that our previous "vacuum" reductions were slightly contaminated, presumably by pump oil which leaked past the cold traps. (3) Contact resistance was lowered considerably by soldering leads to small areas on the faces of the crystals which had been subjected to severe local reduction. (4) When the sample resistance exceeded about a megohm, an electrometer-galvanometer (Keithley Model 610A) was used as the voltage null detector.

The two independent Hall coefficients R_a and R_c for this tetragonal crystal system were measured in the following manner: R_a was obtained with magnetic field along an *a* (twofold) crystal direction and primary current along a crystal *a* or *c* (fourfold) axis; while R_c resulted from magnetic fields and primary currents along the *c* and *a* directions, respectively. Furthermore, R_a measured on both crystals provided an independent check on the amount of reduction or doping for each "pair" of samples.

III. RESULTS

Most of the features of the Hall coefficients and electrical resistivities determined for a large number of *n*-type samples (including four pairs) with ρ_a (300°K) varying from $\sim 10^{-2}$ to 10^6 Ω-cm can be illustrated by data on only a few crystals.

One observes from Table I that the Hall mobilities (R_a/ρ_c or R_c/ρ_a) at 300°K are approximately independent of the carrier concentrations, even when the latter are changed by a factor of 10^6. This is evidence that only properties intrinsic to the crystal are being measured rather than competing extrinsic processes such as surface or impurity conduction (see also Ref. 9).

The temperature dependence of the Hall coefficients (Fig. 1) shows the pronounced features of exponential behavior near room temperature and again at low temperatures (slopes designated ϵ_1 and ϵ_2 in Table I);

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TABLE I. Information concerning samples.

Sample	Orientation	Reduction treatment	ρ[ε] 300°K Ω-cm	R[ζ] 300°K cm^3/C	μ[η] cm^2/V-sec	ϵ_1[θ] eV	ϵ_2[ι] eV
*VR*42*a*	$l\|c$	800°C 7d	6.5×10^4 (*c*)	5×10^4 (*a*)	0.77	0.5 (R_a)	...
		150 Torr (air)[α]				0.42 (ρ_c)	0.11 (ρ_c)
*VR*42*b*	$l\|a$	same	7.5×10^5 (*a*)	...		0.29 (ρ_a)	0.16 (ρ_a)
*VR*43*a*	$l\|c$	800°C 10d	32 (*c*)	33 (*a*)	1.03	0.05 (R_a)	0.048 (R_a)
		2×10^{-7} Torr					0.069 (ρ_c)
*VR*43*b*	$l\|a$	same	2×10^2 (*a*)	51 (*a*)	0.25	0.04 (R_a)	0.05 (R_a)
				46 (*c*)	0.23	0.10 (R_c)	0.04 (ρ_a)
*VR*44*a*	$l\|c$	1000°C 6d	8.8 (*c*)	7.6 (*a*)	0.95	0.046 (R_a)	0.012 (R_a)
		2×10^{-7} Torr					0.011 (ρ_c)
*VR*44*b*	$l\|a$	same	26 (*a*)	7.5 (*a*)	0.29	0.042 (R_a)	
				5.5 (*c*)	0.21		
*VR*23	$l\|a$	1000°C 11d					
		3×10^{-5} Torr[β]					
*VR*28	$l\|c$	800°C 7d	1.2 (*c*)	1.5 (*a*)	1.25	0.040 (R_a)	0.035 (R_a)
		30 Torr[β]					0.033 (ρ_c)
*VR*29	$l\|a$	same	5.9 (*a*)	1.9 (*a*)	0.32	...	0.023 (R_a)
				1.5 (*c*)	0.25		0.027 (ρ_a)
R-1	$l\|a$	800°C 1h	0.3 (*a*)	0.06 (*a*)	0.20	0.06 (R_a)	0.025 (ρ_a)
		760 Torr H_2[γ]		[0.05] (*c*)	0.17		
R-3	$l\|a$	1000°C 1h	6.8×10^{-3} (*a*)	[1.2×10^{-4}] (*a*)	0.18		
		760 Torr H_2[δ]		1×10^{-4} (*c*)	0.15	0.16 (R_c)	0.03 (ρ_a)

[α] Sealed in 9 cc capsule.
[β] Sealed in 5 cc capsule.
[γ] Weight loss 0.14%.
[δ] Weight loss 1.76%.
[ε] ρ measured with the current in the direction as indicated in parentheses.
[ζ] R measured with the magnetic field direction as indicated in parentheses.
[η] Hall mobility (R_a/ρ_c or R_c/ρ_a) see text (III).
[θ] ϵ_1 is the slope of $\ln R_a$, $\ln R_c$, $\ln \rho_a$, or $\ln \rho_c$ versus $1/T$ (at 300°K) as indicated in parentheses.
[ι] ϵ_2 is the slope of $\ln R_a$, $\ln R_c$, $\ln \rho_a$, or $\ln \rho_c$ versus $1/T$ (at low temperatures: ~12°K) as indicated in parentheses.

for intermediate temperatures, either a maximum or inflection in R is observed. Finally, at very low temperatures, another maximum in the Hall coefficient occurs which is due to conduction in impurity levels, as previously discussed.[6,10]

There have been suggestions that the two exponential regions of $\ln R$ versus $1/T$ may represent excitation of electrons to the conduction band from a center capable of donating two electrons (i.e., oxygen vacancy),[11,12] or perhaps from a single donor (such as interstitial Ti^{3+}) with the ionization energy being a function of temperature.[2,13] The present study indicates that the low temperature slope ϵ_2 is due to excitations of electrons to the lowest conduction band from donor centers partly compensated by acceptors.[14,15] Measured values of ϵ_2 have ranged from 0.006 to 0.2 eV. On the other hand, the slopes near 300°K (ϵ_1) are primarily a result of excitations of electrons from the lowest conduction band to a second band whose minimum is 0.05 eV higher in energy. One expects with heavily compensated samples, for which exhaustion of the compensated donor centers is not complete at room temperature, that larger values of ϵ_1 would be observed (i.e., sample *VR*42*a*, $\epsilon_{1a}=0.5$ eV) than in samples with low compensation for which $\epsilon_{1a}=0.05$ eV. Variations

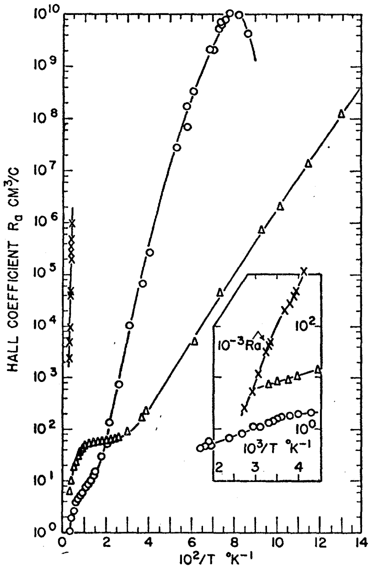

FIG. 1. Hall coefficient R_a versus reciprocal of absolute temperature. The inset shows the data near room temperature and above on an expanded temperature scale.

○-*VR*28;
×-*VR*42a;
△-*VR*44a.

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of ϵ_1 for slightly reduced rutile have also been observed by Acket and Volger.[16]

The temperature dependence of the resistivities (Fig. 2) is described by the above-mentioned electronic excitations taking into account Hall mobilities which increase rapidly as the temperature is decreased.[2,6,7,11,16] For the lightly compensated samples this leads to a smaller resistivity as the temperature is lowered near 300°K, and the opposite temperature dependence for the heavily compensated samples.

The temperature dependences of the other transport quantities R_c and ρ_a are rather similar to those of R_a and ρ_c, respectively. An outstanding feature is that the *ratios* R_c/R_a (or ρ_a/ρ_c) are virtually the same for all samples. From Fig. 3 one notes that R_c/R_a is independent of temperature for $T < \approx 40°\text{K}$; this ratio increases to a maximum value of about 2.5 at 110°K and subsequently decreases at higher temperatures (i.e., $R_c/R_a \approx 0.2$ at 625°K). On the other hand, ρ_a/ρ_c has a nearly constant value of 2.0 at low temperatures, increases (similarly to R_c/R_a) to a maximum vlaue of 4.5 ± 0.5 at 100°K, and decreases more slowly than R_c/R_a at higher temperatures (i.e., $\rho_a/\rho_c \simeq 2.0$ at 625°K).

These results for R_c/R_a and ρ_a/ρ_c versus $1/T$ are in agreement with most of the rather limited data in the literature.[7,16,17] Studies by Bogomolov and Zhuze[7] included the temperature range 78 to 700°K for crystals with ρ_c (300°K) the order of 1 Ω-cm; moreover, from a detailed series of measurements at 300°K, Bogomolov and Shavkunov[17] conclude that ρ_a/ρ_c has practically a constant value of about 3.5, even when the resistivity covers the range 1 to 10^9 Ω-cm. Analysis with a two-conduction-band model (Sec. IV) provides interpretation for the anisotropy of the Hall coefficients and electrical conductivities.

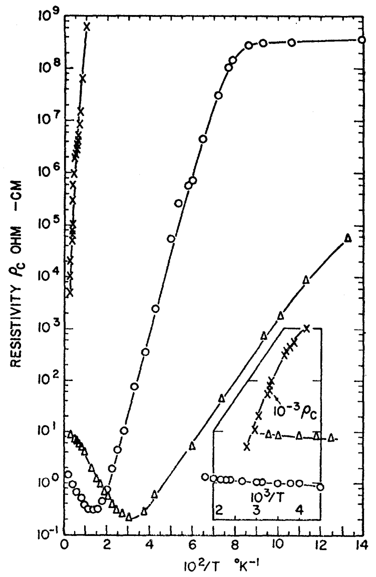

FIG. 2. Electrical resistivity ρ_c versus reciprocal of absolute temperature. The inset shows the data near room temperature and above on an expanded temperature scale.

○-*VR*28;
×-*VR*42*a*;
△-*VR*44a.

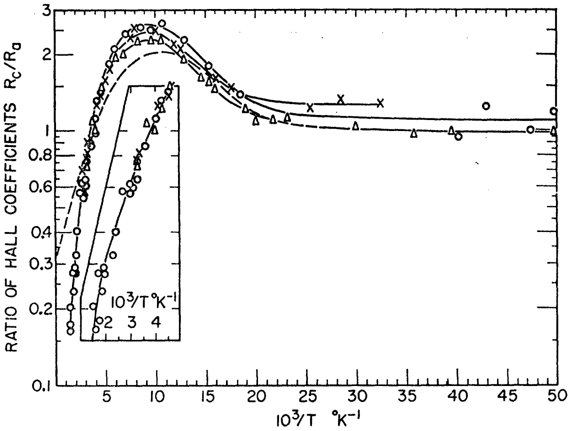

FIG. 3. Hall coefficient anisotropy ratio R_c/R_a versus reciprocal of absolute temperature. The inset shows the data near room temperature. The dashed curve is calculated from Eq. (6) (see text).

×-*VR*23; ○-*VR*29; △-*VR*44*b*.

Two experimental observations will be mentioned which relate to the difficulty of obtaining two samples (i.e., $l\|c$ and $l\|a$) with identical carrier concentrations and mobilities at all temperatures. (1) Frequently, two specimens cut from adjacent portions of a large "homogeneous" boule when reduced together in the same vacuum system do not indicate the same carrier concentrations, even though the times allowed for reduction (≈one week) are more than adequate to achieve thermodynamic equilibrium.[18–21] Samples with a higher proportion of *a-c* surface area (i.e., planes on the surface containing *a* and *c* directions) compared with *a-a* surface area are more reduced. We have no adequate explanation of these observations; however, anisotropic surface free energies or anisotropic diffusion of impurities[18–21] into or out of these crystals might be considered.

(2) Chemisorbed oxygen acts as an acceptor or electron trap; thus, even at room temperature in nearly completely compensated samples, the measuring environment can significantly influence the carrier concentrations, as is well known for many oxides.[22,23]

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[17] V. N. Bogomolov and P. M. Shavkunov, Fiz. Tverd. Tela **5**, 2027 (1963) [English transl.: Soviet Phys.—Solid State **5**, 1481 (1963)].

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Such effects have been demonstrated for high-resistivity rutile by Keezer.[24] Our measurements indicate that the change of carrier concentrations within the depletion layers under the contacts[16–18,25] causes a considerably larger change of contact resistance than bulk resistance. For example, the resistivity of sample *VR*42*a* increased by 7% while the contact resistance (approximately twenty times the sample resistance) was doubled when the environment at room temperature was changed from forepump vacuum to one atmosphere of oxygen. Although the Hall coefficients, resistivities, and contact resistances in highly compensated samples may be altered by chemisorbed oxygen, we have no evidence of any influence on the Hall mobility at 300°K. At low temperatures, where impurity scattering becomes important, one expects the mobility to depend upon the amount of chemisorbed oxygen.

IV. ANALYSIS

In a tetragonal crystal with a *single* broad conduction band, the Hall coefficients and electrical conductivities in zero magnetic field may be expressed as

$$R_a = -r_a/nec. \quad R_c = -r_c/nec, \tag{1}$$

and

$$\sigma_a = ne\mu_a, \quad \sigma_c = ne\mu_c. \tag{2}$$

The r factors (ratio of Hall mobility to drift mobility) have received considerable attention for cubic crystals.[26] For this case $r_a = r_c$ and values are usually rather close to unity; however, relatively little work concerning these factors has been carried out for tetragonal crystals. Several models for energy surfaces in tegragonal crystals have been investigated by Hernandez and Kahn[27] who assumed an isotropic energy-dependent relaxation time τ. They find that r_a and r_c include not only the average of τ and τ^2 over the carrier distribution, but also may vary according to the anisotropy and curvature of the energy bands represented by the factors K_a and K_c where

$$r_a = (\langle\tau^2\rangle/\langle\tau\rangle^2)\,K_a, \quad r_c = (\langle\tau^2\rangle/\langle\tau\rangle^2)\,K_c. \tag{3}$$

For example, a single spheroidal energy surface centered at $\mathbf{k}=0$ would have $K_a = K_c = 1$. However, with four ellipsoids having principal effective masses m_x, m_y, m_z, directed along the crystal axes ($a,a,c,$) they obtain $K_a = 1$, $K_c = 4m_x m_y/(m_x + m_y)^2 \leq 1$. Detailed calculations have not been carried out for the case of anisotropic τ in tetragonal crystals. Studies on cubic[28,29] and hexagonal[29] materials have indicated that the effective masses and relaxation times enter the factor K as $m_i' = m_i/\tau_i$. It seems reasonable to conclude for tetragonal crystals that K_c described above will become $K_c' = 4m_x' m_y'/(m_x' + m_y')^2$ and thus remain equal to or less than unity.

With these concepts in mind, it appears that conduction in a single broad band can not explain the anisotropic Hall coefficient data of Fig. 3, since such an analysis would require R_c/R_a to be roughly a constant and approximately equal to or less than unity. On the other hand, the magnitude and temperature of R_c/R_a are readily accounted for by conduction in two or more anisotropic bands.

For *multiple* broad band conduction in tetragonal crystals, the calculations of Hernandez and Kahn[27] may be written in the form (illustrated for two conduction bands—upper, u, and lower, l):

$$R_a = (R_{la}\sigma_{la}\sigma_{lc} + R_{ua}\sigma_{ua}\sigma_{uc})/(\sigma_{la} + \sigma_{ua})(\sigma_{lc} + \sigma_{uc}), \tag{4}$$

and

$$R_c = (R_{lc}\sigma_{la}^2 + R_{uc}\sigma_{ua}^2)/(\sigma_{la} + \sigma_{ua})^2,$$

with

$$\sigma_a = \sigma_{la} + \sigma_{ua} \quad \text{and} \quad \sigma_c = \sigma_{lc} + \sigma_{uc}. \tag{5}$$

It is interesting that R_c is of the form obtained for cubic materials,[26,29] while R_a contains both principal conductivities. A single derivation of these equations is contained in the Appendix.

The anisotropy ratios are thus

$$R_c/R_a = \frac{r_{lc}(1+AX)(1+CX)}{r_{la}(1+BX)(1+X)} \tag{6}$$

and

$$\sigma_c/\sigma_a = \frac{\mu_{lc}(1+CX)}{\mu_{la}(1+X)}, \tag{7}$$

where X is defined as σ_{ua}/σ_{la} and the factors A, B, and C equal Hall and drift mobility ratios of the upper band relative to those of the lower band and are given by

$$A = r_{uc}\mu_{ua}/r_{lc}\mu_{la}, \quad B = r_{ua}\mu_{uc}/r_{la}\mu_{lc},$$
$$C = \mu_{uc}\mu_{la}/\mu_{lc}\mu_{ua} = Br_{la}r_{uc}/Ar_{ua}r_{lc}. \tag{8}$$

With this model, at sufficiently low temperatures ($T < 40$°K), conduction will take place predominantly in the lowest band and the Hall-coefficient anisotropy ratio R_c/R_a will equal r_{lc}/r_{la}, which should be approximately a constant equal to or less than unity. From Fig. 3 and similar data on other crystals we conclude $r_{lc}/r_{la} = 1.0 \pm 0.1$.

The magnitude and temperature dependence of the conductivity ratio $X(\equiv\sigma_{ua}/\sigma_{la})$ emerges from the

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[25] R. A. Parker and J. H. Wasilik, Phys. Rev. **120**, 1631 (1960).

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[27] W. C. Hernandez, Jr. and A. H. Kahn, J. Res. Natl. Bur. Std. **67A**, 293 (1963).

[28] C. Herring, Bell System Tech. J. **34**, 237 (1955); also C. Herring and E. Voight, Phys. Rev. **101**, 944 (1956).

[29] For a comprehensive review, see A. C. Beer, *Solid State Physics—Supplement 4*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1963).

following calculation which also yields the energy difference between the two conduction bands (E_u-E_l). Since

$$\sigma_{ua}/\sigma_{la}=(\mu_{ua}N_u/\mu_{la}N_l)\exp[-(E_u-E_l)/kT], \quad (9)$$

where N_u and N_l are the density of states in the upper and lower bands, respectively, it is clear that this ratio approaches zero at low temperatures ($kT\ll E_u-E_l$). Expanding R_c/R_a from Eq. (6) with $r_{lc}/r_{la}=1$, one obtains for small X

$$\frac{R_c}{R_a}-1\approx(A+C-B-1)\times\frac{\mu_{ua}N_u}{\mu_{la}N_l}\exp[-(E_u-E_l)/kT]. \quad (10)$$

If we assume that for small temperature changes (≈ 10°K) the mobility and density-of-state ratios do not vary significantly in comparison with the exponential term, then a plot of $\ln(R_c/R_a-1)$ at low temperatures should exhibit a linear dependence on $1/T$, with a slope equal to $(E_u-E_l)/k$. From such data we obtain a separation of the conduction band minima ranging from 0.04 to 0.06 eV; the corresponding pre-exponential factor of Eq. (10), (PE), varies between 4×10^3 and 10^6. The conductivity ratio X may thus be estimated from

$$X=\frac{(\mathrm{PE})}{A+C-B-1}\exp[-(E_u-E_l)/kT]. \quad (11)$$

At higher temperatures excitations of electrons will take place from the lower conduction band and compensated donor levels to the upper conduction band. It can be shown that such excitations qualitatively describe the temperature dependence of the Hall coefficient anisotropy (Fig. 3). This requires appropriate choices of values for the mobility ratios A, B, and C. These parameters were selected by fitting the magnitude of R_c/R_a at two temperatures, namely, 110°K, where the maximum anisotropy is found, and 265°K, where the anisotropy has decreased to unity. The dashed curve of Fig. 3 is an example of a qualitative fit. The values $A=0.010$, $B=4.2$, and $C=17$ with $E_u-E_l=0.030$ eV were used in the calculations. Increasing the magnitude of E_u-E_l from 0.03 to 0.06 eV gives considerably better agreement at the high temperatures, but a larger discrepancy at low temperatures. Unfortunately, even with the most appropriate estimate of the band separation, the choice of the mobility ratios A, B, and C is not unique. As may be seen from Eq. (6), R_c/R_a is the same irrespective of whether the mobility ratios A and C are interchanged or B equals a certain value or its reciprocal; however, the large (or small) values of A, B, and C required to qualitatively fit the data indicate that the energy bands are rather anisotropic. Support for this conclusion also comes from the magnitude of R_c/R_a at the highest temperatures. In order for this quantity to be small, it is necessary that r_{uc}/r_{ua} ($\leq R_c/R_a$ at high temperature) also be much less than unity, which implies the upper conduction band is very anisotropic and the simple considerations mentioned previously imply at least four ellipsoids for this band.

Although, for temperatures higher than 40°K, the above considerations demonstrate the plausiblity of multiple-band conduction in n-type rutile, detailed considerations concerning the effective masses, bandwidths, mobilities, and their temperature dependence require a more extensive analysis. Unfortunately, even the density of states in the lowest conduction band is difficult to estimate from Hall coefficient and thermoelectric power data below 40°K, since a large phonon-drag effect greatly exceeds the electronic contribution to the thermoelectric power.[30]

ACKNOWLEDGMENTS

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APPENDIX: EQUATIONS FOR THE HALL COEFFICIENTS R_a AND R_c OF TETRAGONAL CRYSTALS WITH MULTIPLE-CONDUCTION BANDS

The equations for the Hall coefficients of a crystal with multiple conduction bands can be readily expressed in terms of the Hall coefficients and electrical conductivities of each band. The Hall coefficient is defined as $R\equiv\epsilon_y{}^H/j_xH_z$, where $\epsilon_y{}^H$ is the transverse electric (Hall) field resulting from a primary current density j_x and a magnetic field H_z. The Hall field $\epsilon_y{}^H$ may be written in terms of the short circuit Hall current density j_y and electrical conductivity (in the direction of the Hall current)[31] since $\epsilon_y{}^H=j_y{}^H/\sigma_y$.

To obtain the Hall coefficients R_a and R_c for tetragonal crystals, we will consider the sample geometries described in Sec. II. We calculate R_a with primary current flow (density j_a) along a crystal a axis, and magnetic field along the other crystal a axis (H_a); thus, the Hall field $\epsilon_c{}^H$ (or Hall current density $j_c{}^H$) is developed along the third direction or crystal c axis. The Hall coefficient R_a can thus be derived from

$$R_a=\epsilon_c{}^H/j_aH_a=j_c{}^H/\sigma_cj_aH_a. \quad (\mathrm{A1})$$

For a two conduction-band system the short-circuit Hall current density $j_c{}^H$ is the sum of the contributions of each band, i.e., $j_c{}^H=j_{lc}{}^H+j_{uc}{}^H$. These are each equal to the primary current density carried by each

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[30] W. R. Thurber and H. P. R. Frederikse, Bull. Am. Phys. Soc. **9**, 49 (1964); W. R. Thurber, M. S. thesis, University of Maryland, 1963 (unpublished).

[31] A similar relationship is commonly employed in calculating the open-circuit PME voltage in terms of the short-circuit PME current, i.e., W. Van Roosbroeck, Phys. Rev. **101**, 1713 (1956).

band times the Hall angle of that band, i.e.,

$$j_{lc}{}^H=\theta_{lc}j_{la}=(R_{la}\sigma_{lc}H_a)j_{la}$$

and

$$j_{uc}{}^H=\theta_{uc}j_{ua}=(R_{ua}\sigma_{uc}H_a)j_{ua}\,. \qquad \text{(A2)}$$

We have used the relation for weak magnetic fields that for each band the tangent of the Hall angle is equal to the Hall angle, and that the Hall angle equals the Hall mobility (in the direction of the Hall field) times the magnetic field.[32]

The primary current densities carried by each band j_{la} and j_{ua} are a fraction of the total primary current density, j_a given by

$$j_{la}=[\sigma_{la}/(\sigma_{la}+\sigma_{ua})]j_a\,,$$

$$j_{ua}=[\sigma_{ua}/(\sigma_{la}+\sigma_{ua})]j_a\,, \qquad \text{(A3)}$$

where we assume intervalley scattering is sufficiently weak so as not to break down the additivity relationship, $\sigma=\sigma_l+\sigma_u$. Inserting Eqs. (A2) and (A3) into Eq. (A1), and using the relationship $\sigma_c=\sigma_{lc}+\sigma_{uc}$, one obtains Eq. (4) of the text, namely,

$$R_a=\frac{R_{la}\sigma_{lc}\sigma_{la}+R_{ua}\sigma\pi_c\sigma_{ua}}{(\sigma_{lc}+\sigma_{uc})(\sigma_{la}+\sigma_{ua})}\,. \qquad \text{(A4)}$$

For determination of R_c the primary current is again taken along a crystal *a* axis (i.e., j_a), but now the magnetic field is along a crystal *c* axis (H_c); thus, the Hall field is developed along the other crystal *a* axis ($\epsilon_a{}^H$). The equation analogous to (A1) is

$$R_c=\epsilon_a{}^H/j_aH_c=j_a{}^H/\sigma_aj_aH_c\,. \qquad \text{(A5)}$$

Similarly, instead of Eqs. (A2) we obtain

$$j_{la}{}^H=\theta_{la}j_{la}=(R_{lc}\sigma_{la}H_c)j_{la}$$

and

$$j_{ua}{}^H=\theta_{ua}j_{ua}=(R_{uc}\sigma_{ua}H_c)j_{ua}\,. \qquad \text{(A6)}$$

By combining Eqs. (A5), (A6), and (A3) with $\sigma_a=\sigma_{la}+\sigma_{ua}$, one obtains Eq. (4) of the text for R_c, namely,

$$R_c=\frac{R_{lc}\sigma_{la}{}^2+R_{uc}\sigma_{ua}{}^2}{(\sigma_{la}+\sigma_{ua})^2}\,. \qquad \text{(A7)}$$

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[32] The applicability of the Hall mobility in the direction of the Hall field is apparent from more formal derivations (Refs. 25–28) and may be readily demonstrated by calculating R_a with an alternative geometry, i.e., both primary current and magnetic fields along *a* directions of the crystal.

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Perturbation Treatment of the Antiferromagnetic Ground State*

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Ground-state parameter series expansions are generated for the Heisenberg model of antiferromagnetism. These expansions are taken about the Ising model, and the terms are expressed as analytic functions of the spin for the linear chain, plane quadratic, simple cubic, body-centered cubic, and hypercubic lattices. Energy, short-range order, and sublattice magnetization series are given through fourth order in the transverse spin operators, and numerical values are calculated for these terms in the cases of the linear chain, plane quadratic, simple cubic, and body-centered cubic lattices with $2S=1, 2, 3, 4, 5$. Comparison is made with the ground-state parameter series developed for a spin-wave theory with Ising anisotropy, and an "overlap" contribution common to both treatments is defined. It is found that the disagreement between the spin-wave theory of the ground-state sublattice magnetization and the experimental results for $KMnF_3$ and MnF_2 is not contradicted by our perturbation treatment.

I. INTRODUCTION

WITHIN the past few years, there has been a great deal of activity concerning the properties of the ground state of the Heisenberg antiferromagnet. (For a partial list, see Refs. 1–12.) Recently, measurements of the sublattice magnetization of the ground state of some real antiferromagnets, i.e., MnF_2[13,14] and $KMnF_3$,[15] have provided interesting tests for these theories. The results so far indicate that there remains an unexplained dis-

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