THE RADIATIVE PARAMETERS OF SOLIDS*

B. A. Khrustalev

UDC 536.3:535.34

Research on the radiative behavior of solids is surveyed. Radiation parameters are classified, the state of the theory is surveyed, and details are given of the state of knowledge on primary and average radiative parameters of solids. Radiative behavior is examined as regards use in engineering calculations.

1. Basic Equations of Radiation Transport and Classification of Radiative Parameters. The radiative parameters of solids are receiving increasing attention from scientists, engineers, and designers; there is a steadily increasing flow of papers on radiation by solids and radiative energy transport in solids.

These features are due to the part played by radiative transport in high-temperature heat exchangers, combustion chambers, steam boilers and metallurgical furnaces, flying vehicles, and vacuum and space-research equipment generally.

Reliable calculation of radiative transfer is impossible without a knowledge of the radiative thermophysical parameters of materials and media.

The radiative properties of a solid are the thermophysical properties that characterize the interaction of the solid with electromagnetic radiation during energy transfer.

These properties will be examined via the basic equations of radiation transport, which form the basis of radiative heat transfer [1].

Radiation transport in a body is described by

$$\frac{\partial I_\nu(s)}{\partial s}+\frac{1}{c_0}n_\nu\frac{\partial I_\nu(s)}{\partial t}=\alpha'_\nu n_\nu^2\frac{E_{0\nu}}{\pi}-(\alpha'_\nu+\beta_\nu)I_\nu(s)+\frac{\beta_\nu}{4\pi}\int\limits_{4\pi}I_\nu(s')\gamma_\nu(s',\ s)\,d\Omega', \tag{1}$$

and at the boundary by

$$I_{e\nu}(s)=\varepsilon_\nu(s)n_\nu^2\frac{E_{0\nu}}{\pi}+\frac{1}{\pi}\int\limits_{+2\pi}I_{n\nu}(s')\cos\widehat{(s'n)}\,r_\nu(s')\,p_\nu(s',\ s)\,d\Omega'. \tag{2}$$

These equations contain the primary radiation characteristics, which include the bulk primary characteristics: $n_\nu = c_0/c_\nu$ the spectral refractive index of the medium with respect to vacuum (ratio of the speed of radiation in vacuum to that in the medium); $\alpha'_\nu = \alpha_\nu[1-\exp(-h\nu/kT)]$ the effective spectral absorption coefficient of the medium (including induced emission); α_ν the absorption coefficient of the medium; β_ν the spectral coefficient of the scattering of the medium; and $\gamma_\nu(s', s)$ the spectral scattering indicatrix. There are also the boundary radiation characteristics: $\varepsilon_\nu(s)$ the spectral emissivity at point N in the direction s; $r_\nu(s')$ the spectral reflection coefficient of an elementary area for radiation incident from direction s'; and $p_\nu(s', s)$ the reflection indicatrix (indicatrix for surface scattering) of an elementary area.

* The paper is based on a review paper read in May, 1969 in Leningrad at the meeting of the Radiative Heat-Transfer section of the Council on Mass and Heat Transfer in Technological Processes, Council of Ministers of the USSR. This meeting was concerned with the use of the radiative properties of solids.

Krzhizhanovskii Power Institute. Moscow. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 18, No. 4, pp. 740-762, April, 1970. Original article submitted November 27, 1969.

These characteristics (n_ν, α_ν, β_ν, γ_ν, ε_ν, r_ν, p_ν) are primary ones because they allow us to calculate all the integral, average, and effective ones.

Equations (1) and (2) are used in radiation-transport calculations if one needs to take into account the variation in properties with direction, wavelength, etc.; but most current design calculations on radiative transfer use mean energy fluxes and the corresponding average radiation characteristics.

For instance, we have the equation for conservation and transformation of radiation energy:

$$\frac{\partial u}{\partial t} + \operatorname{div} \mathbf{q} = 4\alpha'_{\text{me}} n^2 \sigma_0 T^4 - \alpha' c u \tag{3}$$

and the equations relating the effective, incident, and resultant radiation fluxes at the boundary surface:

$$E_e = \varepsilon n^2 \sigma_0 T^4 + r E_i, \tag{4}$$

$$E_p = a E_i - \varepsilon n^2 \sigma_0 E, \tag{5}$$

which are derived by integrating (1) and (2) over the spectrum and space, and which contain the following average characteristics:

$\alpha'_{\text{me}} = \int_0^\infty \alpha'_\nu n_\nu^2 E_{0\nu} d\nu \Big/ \int_0^\infty n_\nu^2 E_{0\nu} d\nu$ is the Planck mean emission coefficient taken over all frequencies;

$\alpha' = \int_0^\infty \alpha'_\nu d\nu \int_{4\pi} I_\nu(\mathbf{s})\, d\Omega \Big/ \int_0^\infty d\nu \int_{4\pi} I_\nu(\mathbf{s})\, d\Omega$ is the absorption coefficient averaged over all frequencies and directions;

$n^2 = \int_0^\infty n_\nu^2 E_{0\nu} d\nu \Big/ \int_0^\infty E_{0\nu} d\nu$ is the square of the refractive index averaged over all frequencies;

$\varepsilon = \int_0^\infty n_\nu^2 E_{0\nu} d\nu \int_{-2\pi} \varepsilon_\nu(\mathbf{s}) |\cos \widehat{(sn)}|\, d\Omega \Big/ \pi \int_0^\infty n_\nu^2 E_{0\nu} d\nu$ is the total hemispherical emissivity of the boundary surface;

$r = \dfrac{\int_0^\infty d\nu \int_{+2\pi} I_{n\nu}(\mathbf{s}') \cos \widehat{(s'n)}\, r_\nu(\mathbf{s}')\, d\Omega'}{\int_0^\infty d\nu \int_{+2\pi} I_{n\nu}(\mathbf{s}') \cos \widehat{(s'n)}\, d\Omega'}$ is the total hemispherical emissivity (reflection coefficient); and

$a = 1 - r$ is the total hemispherical absorbing power of the surface.

We will not consider how to average the other quantities in (3)-(5) because they are not involved in the present discussion.

If other approximate or averaged expressions are used in calculating radiative heat transfer, one obtains other rules for averaging the radiation characteristics. For instance, the diffusion representation for the radiation-flux vector gives rise to the Rosseland mean emission coefficient [2, 3]; again, a tensor approximation gives the more complex Adrianov mean [1].

The mean characteristics α', r, and a have the important feature that they are not physical properties of the material; the other radiation characteristics are such and are dependent on the form of the material, the parameters of the thermodynamic state, and the structure. They are functionals, since they depend not only on the above factors but also on the spatial distribution of the radiation fluxes and thus vary with the detailed conditions in an engineering problem.

This feature means that one must examine the conditions of derivation of these mean characteristics and compare them with the conditions of the detailed problem in order to establish whether they are applicable.

We now consider our knowledge of these characteristics for solids.

2. Primary Radiation Characteristics. The most important are n_ν (the refractive index) and k_ν (the absorption index); the latter is related to the absorption coefficient α_ν by

$$\alpha_\nu = \frac{4\pi k_\nu}{\lambda}. \tag{6}$$

These coefficients characterize the interaction of electromagnetic radiation with matter and indicate how the propagation speed varies and how the amplitude decays; they are termed the basic optical parameters of the body.

Theoretical principles for deriving n_ν and k_ν were derived long ago within the electromagnetic theory of radiation, the classical electronic theory, and the quantum theory of solids. The basis has latterly been considerably extended via the theory of the solid state.

The classical electromagnetic theory [4] for radiation is based on Maxwell's equations:

$$\begin{gathered}\operatorname{rot}\mathbf{E} = -\frac{1}{c}\frac{\partial \mathbf{B}}{\partial t},\\ \operatorname{rot}\mathbf{H} = \frac{4\pi}{c}\mathbf{j} + \frac{1}{c}\frac{\partial \mathbf{D}}{\partial t},\\ \operatorname{div}\mathbf{B} = 0,\\ \operatorname{div}\mathbf{D} = 4\pi f\end{gathered} \tag{7}$$

and on the phenomenological relations between the induction and current vectors on the one hand and the electric and magnetic field ones on the other:

$$\begin{aligned}\mathbf{D} &= \varepsilon_d \mathbf{E},\\ \mathbf{B} &= \mu \mathbf{H},\\ \mathbf{j} &= \sigma \mathbf{E}.\end{aligned} \tag{8}$$

These equations may be solved for the electric and magnetic fields in the radiation and also for n_ν and k_ν, i.e.,

$$\begin{gathered}\varepsilon_d \mu = n_\nu^2 - k_\nu^2,\\ \sigma\mu = n_\nu k_\nu \nu,\\ n_\nu^2 = \frac{\mu}{2}\left[\sqrt{\varepsilon_d^2 + 4\left(\frac{\sigma}{\nu}\right)^2} + \varepsilon_d\right]\end{gathered} \tag{9}$$

or

$$k_\nu^2 = \frac{\mu}{2}\left[\sqrt{\varepsilon_d^2 + 4\left(\frac{\sigma}{\nu}\right)^2} - \varepsilon_d\right],$$

which relate n_ν and k_ν to the electric and magnetic parameters ε_d and μ, as well as the specific electrical conductivity σ.

Maxwell's theory does not reveal what controls ε_d, μ, and σ; the electronic and quantum theories of the solid state are required to give the dependence on the frequency ν.

The classical electronic theory deals with the interaction of electromagnetic waves with the outer (optical) electrons in the atoms [6-9].

Lorenz [6] considered the motion of an electron bound to the material by elastic forces in response to a periodic electric field, and he derived dispersion formulas for σ and ε_d:

$$\begin{aligned}\sigma &= \frac{N_e e^2}{m}\frac{\omega^2\gamma}{(\omega_i^2 - \omega^2)^2 + \gamma^2\omega^2},\\ \varepsilon_d &= 1 + 4\pi\frac{N_e e^2}{m}\frac{\omega_i^2 - \omega^2}{(\omega_i^2 - \omega^2)^2 + \gamma^2\omega^2},\end{aligned} \tag{10}$$

in which ω_i is the circular frequency of the free vibration of an elastically bound electron and $\omega = 2\pi\nu$ is the circular frequency of the radiation.

Drude, Kronig, Zener, and others considered a free-electron model for metals. The Drude–Zener formulas are derived from (10) by putting $\omega_i = 0$, and the Drude–Zener model explains some observed properties; it applies to the longwave region (low frequencies), but in the shortwave region (near infrared, visible, and ultraviolet) the electrons interact with: 1) the ionic lattice; 2) one another; 3) electrons in deeper shells, so the theory does not apply to these regions.

Mott and Jones [10] extended the theory by incorporating the photoelectric effects and the polarization of the deeper electron shells in atoms.

Roberts [11] took into account bound electrons and several types of free electrons to improve Drude's theory, and thus derived the optical parameters of nickel and tungsten in the visible region ($T < 1600°$).

The quantum theory of the optical parameters deals in detail with the dispersion due to these interactions; it is based on the quantum theory of the solid state. There are several dispersion formulas for the visible and ultraviolet regions for metals, alloys, ferromagnetics, semiconductors showing the anomalous skin effect, etc., which have been deduced by various workers [4, 12, 13].

The Kramers–Kronig dispersion relation between n_ν and k_ν is an important one, since one can be deduced if the other is known over a wide range [5, 14]:

$$n_{\nu_1} = 1 + \frac{2}{\pi}\int_0^\infty \frac{\nu k_\nu}{\nu^2 - \nu_1^2}\, d\nu. \tag{11}$$

This is the position as regards the physical principles of the optical properties of solids, but we have only rather restricted concrete data on n_ν and k_ν for technical materials, e.g., n_ν and k_ν for some metals and insulators in the visible and near-infrared regions, mostly for room temperature [15-19, 37]. It is an important feature of research on the radiation properties of solids to derive n_ν and k_ν for technical materials over wide spectral and temperature ranges.

Also, n_ν and k_ν govern other important parameters: bulk ones β_ν, $\gamma_\nu(\mathbf{s}', \mathbf{s})$ and boundary ones $\varepsilon_\nu(\mathbf{s})$, $r_\nu(\mathbf{s})$, $p_\nu(\mathbf{s}', \mathbf{s})$.

The bulk ones are the scattering coefficient β_ν and the scattering indicatrix $\gamma_\nu(\mathbf{s}', \mathbf{s})$ which have been examined mainly for powder media; theoretical principles have been devised [20, 21] for calculating them. They depend not only on n_ν and k_ν but also on d/λ, the ratio of the inhomogeneity parameter to the wavelength. Blokh [22] has used scattering calculations for such media in heat engineering. Adrianov and others [23-27] have shown that scattering influences radiative heat transfer.

However, scattering is important not only for powder-based media, since Lapina has shown that scattering determines to a large extent the emissivity of certain solid insulators, including oxide cathodes.

Various other papers [24, 29, 30] deal with the effects of β_ν and $\gamma_\nu(\mathbf{s}', \mathbf{s})$ on the radiative parameters of solids.

Handbooks and the technical literature lack almost entirely data on β_ν and $\gamma_\nu(\mathbf{s}', \mathbf{s})$ for technical materials (insulators, oxides) in which scattering dominates the radiative heat transfer, primarily because no methods are available for direct measurement of β_ν, and most methods give instead $(\alpha'_\nu + \beta_\nu)$. The scattering coefficients presently in use are derived by calculation.

We now consider $\varepsilon_\nu(\mathbf{s})$, $r_\nu(\mathbf{s})$, and $p_\nu(\mathbf{s}', \mathbf{s})$, which are characteristics related to the behavior of radiation at the boundary of a body.

Fresnel's formulas for the magnitudes of the reflected and refracted fluxes [4, 31, 49] are derived by considering the reflection and refraction of electromagnetic radiation at the boundary on the basis of Maxwell's equations, while Snell's formula gives the direction of propagation.

Fresnel's formulas give the reflection coefficient (spectral directional reflectivity) at a surface. The reflected radiation is polarized [50, 51].

The mean reflection coefficients consist of the reflection coefficients for radiation polarized in planes parallel and perpendicular to the plane of incidence:

$$r_\nu(s') = \frac{1}{2}\left[r_\perp(\theta') + r_\parallel(\theta')\right]. \tag{12}$$

The surface is considered as being smooth (scattering absent). The direction s' of the incident ray is here defined by the polarization angle θ'.

The following are [32-36] the polarized components of the reflectivity:

$$r_\perp(\theta') = \frac{(n_\nu - \cos\theta')^2 + n_\nu\left[(1+k_{0\nu}^2)\,\alpha - \beta^2\right]}{(n_\nu + \cos\theta')^2 + n_\nu\left[(1+k_{0\nu}^2)\,\alpha - \beta^2\right]}; \tag{13}$$

$$r_\parallel(\theta') = \frac{\left[n_\nu\zeta - \alpha(\cos\theta')^{-1}\right]^2 + n_\nu^2\left[(1+k_{0\nu}^2)\,\alpha - \zeta^2\right]}{\left[n_\nu\zeta + \alpha(\cos\theta')^{-1}\right]^2 + n_\nu^2\left[(1+k_{0\nu}^2)\,\alpha - \zeta^2\right]},$$

where

$$\alpha^2 = \left[1 + \left(\frac{\sin^2\theta'}{n_\nu^2(1+k_{0\nu}^2)}\right)\right]^2 - \frac{4}{(1+k_{0\nu}^2)}\left[\frac{\sin^2\theta'}{n_\nu^2(1+k_{0\nu}^2)}\right];$$

$$\beta^2 = \frac{(1+k_{0\nu}^2)}{2}\left[\frac{1-k_{0\nu}^2}{1+k_{0\nu}^2} - \frac{\sin^2\theta'}{n_\nu^2(1+k_{0\nu}^2)} + \alpha\right];$$

$$\zeta = \frac{1-k_{0\nu}^2}{1+k_{0\nu}^2}\,\beta + \frac{2k_{0\nu}}{1+k_{0\nu}^2}\left[(1+k_{0\nu}^2)\,\alpha - \beta^2\right]^{1/2};$$

$$k_{0\nu} = k_\nu/n_\nu.$$

We see from (12) and (13) that the reflectivity is governed by n_ν, k_ν, and θ'; Fig. 1 shows this dependence for $r_\nu(s')$ and the components $r_\perp(\theta')$ and $r_\parallel(\theta')$ for insulators and metals.

The directional spectral absorptivity is usually derived from the energy balance:

$$r_\nu(s') + a_\nu(s') + \tau_\nu(s') = 1. \tag{14}$$

The absorptivity and the reflectivity sum to unity for an optically thick body:

$$a_\nu(s') = 1 - r_\nu(s').$$

Kirchoff's laws are obeyed very precisely [3, 38-40] by the spectral directional characteristics, and they give the directional spectral emissivity or degree of blackness:

$$\varepsilon_\nu(s') = a_\nu(s') = 1 - r_\nu(s'). \tag{15}$$

From (12) and (13) we readily get particular formulas for $\theta' = 0$ (normal incidence), for insulators ($k_\nu = 0$), etc. [32, 33].

The formulas for $\varepsilon_\nu(s')$ have been tested by experiment, e.g., $\varepsilon_\nu(\theta')$ [41] for a smooth plate of alumina agreed precisely with that calculated from Fresnel's formula for the known n_ν. The effects of roughness and wavelength were also examined, but no quantitative formulas incorporating the roughness were derived.

Drude and others [7, 42, 43] derived a simplified expression for metals on the basis of Drude's theory. For metals at low frequencies one has

$$\frac{\sigma}{\nu} \gg \varepsilon_0. \tag{16}$$

Then (9) gives

$$n_\nu \simeq k_\nu \simeq \sqrt{\frac{\sigma}{\nu}} = \sqrt{\frac{30\lambda}{\rho}}. \tag{17}$$

From (17) we get the Hagen–Rubens formulas, which were later averaged and revised [45-48]. These formulas take the following form for the spectral directional degree of blackness:

$$\varepsilon_\nu(\theta') = 1 - \frac{1}{2}\left[\frac{60\frac{\lambda}{\rho} - 2\sqrt{\frac{30\lambda}{\rho}}\cos\theta' + \cos^2\theta'}{60\frac{\lambda}{\rho} + 2\sqrt{\frac{30\lambda}{\rho}}\cos\theta' + \cos^2\theta'} + \frac{60\frac{\lambda}{\rho}\cos^2\theta' - 2\sqrt{\frac{30\lambda}{\rho}} + 1}{60\frac{\lambda}{\rho}\cos^2\theta' + 2\sqrt{\frac{30\lambda}{\rho}} + 1}\right]. \quad (18)$$

For the normal direction

$$\varepsilon_\nu(0) = 0.365\sqrt{\frac{\rho}{\lambda}} - 0.0464\frac{\rho}{\lambda} \quad (19)$$

or more precisely

$$\varepsilon_\nu(0) = 0.365\left(\frac{\rho}{\lambda}\right)^{1/2} - 0.0667\left(\frac{\rho}{\lambda}\right) + 0.006\left(\frac{\rho}{\lambda}\right)^{3/2} - 0.004\left(\frac{\rho}{\lambda}\right)^{5/2}.$$

These formulas explain the observed wavelength dependence of ε_ν, but their use is restricted to $\lambda > 10\ \mu$ [4, 32, 33, 43, 52, 53] if one employs the static conductivity σ_S (or resistance ρ_S) in place of the optical value. Sometimes [11, 61, 63, 82] the range of application has been extended to the near infrared. Drude's optical conductivity differs from the static one at short wavelengths (high frequencies) and is related to the latter by

$$\sigma = \frac{1}{\rho} = \frac{\gamma^2}{\omega^2 + \gamma^2}\sigma_S. \quad (20)$$

Also, quantum effects and electron interactions make this formula and the Hagen–Rubens formula inapplicable at short wavelengths.

These formulas give correctly the trend of ε_ν with λ in the infrared but represent the temperature dependence of ε_ν incorrectly; they do not predict the inversion of the temperature dependence observed for metals [53-56] (Fig. 2), and so attempts have been made to derive formulas that agree better with experiment, e.g., Sadykov's formula, where ε_ν is expressed in terms of the thermal conductivity $\varkappa$ and the temperature T [58]:

$$\varepsilon_{\nu,T} = p\sqrt{\frac{T}{\varkappa\lambda}\left(1 + \frac{q^2}{\lambda^2 T^2}\right)}. \quad (21)$$

Although this formula does give such an inversion, the result is not quantitatively correct.

Dmitriev [57] made a new approach to this problem via the interaction with the collective electrons, which are elastically bound to the ionic lattice and which have a natural plasma frequency ν_p. A statistical treatment gave the distribution for the radiation density in the metal as the product of: 1) a Fermi–Dirac function for the electron energy; 2) a Bose–Einstein function for the photon energy, the result being

$$u(\nu, T) = 2\left[\exp\left(-\frac{\varepsilon_1 - \mu_1}{kT}\right) + 1\right]^{-1}\frac{8\pi h\nu^3}{c^3}\left[\exp\left(\frac{h\nu}{kT}\right) - 1\right]^{-1}. \quad (22)$$

Transfer to radiation at the surface gives the degree of blackness as

$$\varepsilon(\nu, T) = \frac{1}{3}\left\{2\left[\exp\left(\frac{h\nu_p}{2kT}\cos\varphi\right) + 1\right]^{-1}\right\}^{2/3}, \quad (23)$$

where

$$\cos\varphi = \frac{\nu_p^2 - \nu^2}{\sqrt{(\nu_p^2 - \nu^2)^2 + \gamma^2\nu^2}}.$$

The inversion then occurs at ν_p, where ε_ν is 1/3. The available evidence is in satisfactory agreement with this [56].

The foreign literature discusses the existence and cause of the x point [54, 55], but no clear explanation of the inversion is given. Dmitriev's formula explains the behavior of the temperature dependence of ε_ν.

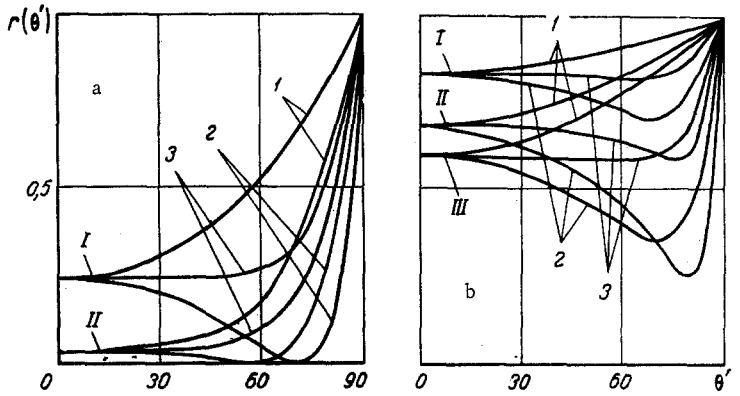

Fig. 1. Spectral reflectivity as a function of direction for: a) insulators [for $k_\nu = 0$; I) $n_\nu = 3.0$; II) 1.5]; b) metals [1) $n_\nu = 0.5$; $k_\nu = 3.0$; II) 3.5; 5.0; III) 1.5; 3.0]: 1) $r_\perp$; 2) $r_\parallel$; 3) r_ν.

An x point occurs not only for metals but also for certain other materials, e.g., zirconium and tantalum carbides or zirconium and hafnium nitrides [53, 60], but $\varepsilon\nu_x$ for these is larger.

Present theoretical studies on these directional spectral characteristics thus enable one to calculate them only for smooth homogeneous materials with known n_ν and k_ν, and not much is known about these quantities for technical materials.

Dmitriev's formula provides a theoretical basis for extrapolation for metals, and this does not contain these quantities in explicit form.

Direct measurement at present remains the principal source of evidence on $r_\nu(s)$ and $\varepsilon_\nu(s)$ for technical materials. Only in recent years has there been any extensive study of these quantities for constructional materials. The fullest results on ε_ν for wide ranges in λ and T have been obtained for some heat-resisting and precious metals [56, 60-65]; less is known about insulators and other constructional materials, and measurements of r_ν and ε_ν for these are needed over wider ranges in λ and T in order to derive general formulas suitable for design calculations.

The reflection indicatrix $p_\nu(s', s)$ is another important characteristic, which is analogous to the bulk scattering indicatrix $\gamma_\nu(s', s)$ and characterizes the distribution of the radiation incident in a direction s' and reflected in space along the direction s (Fig. 3). The form of $p_\nu(s', s) = p_\nu(\theta', 0; \theta, \varphi; h_{rm}/\lambda, T)$ is dependent on λ, T, and the surface roughness; the distribution becomes more even as the roughness increases, with $p_\nu(s', s) = 1$ for a diffusely reflecting surface and $p_\nu = \infty$ for a mirror [66].

There have been several studies on $p_\nu(s', s)$, which have [67, 69] related $p_\nu(s', s)$ to λ and roughness a_r. The reflection approaches specular as a_r/λ decreases.

It has been found [68] that there is a reflection peak at large angles of incidence on a rough surface, which lies at an angle of reflection considerably greater than the specular angle. Torrance gave a theoretical explanation of this.

The bidirectional reflectivity $\rho_{ba}(\theta', \varphi'; \theta, \varphi; T, \lambda)$ is used [33, 35, 67, 68] in the American literature to characterize the distribution of the reflected flux, which is related to $r_\nu(s')$ and $p_\nu(s', s)$ by

$$\pi\rho_{ba}(s', s) = r_\nu(s')\, p_\nu(s', s). \tag{24}$$

The product of $r_\nu(s')$ and $p_\nu(s', s)$ is usually [66, 70] called the brightness coefficient.

Use is also made of the bidirectional reflectivity as a ratio to the value for the specular direction:

$$\frac{\rho_{ba}(\theta', 0; \theta, \varphi)}{\rho_{ba}(\theta', 0; -\theta', 0)} = \frac{p_\nu(s', s)}{p_\nu(s', s_e)}, \tag{25}$$

i.e., the relative indicatrix.

In the USSR there have also been several studies on p_ν, especially Shcherbina's [72] on the effects of T, λ, and roughness on the shape of the indicatrix for various materials in normal incidence. The effects of T were found to be slight.

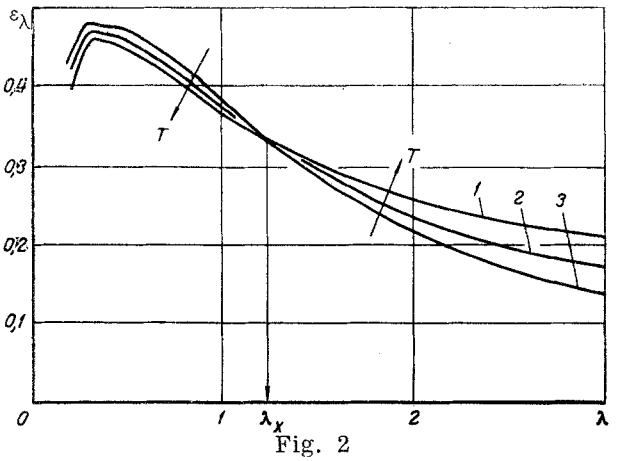

Fig. 2

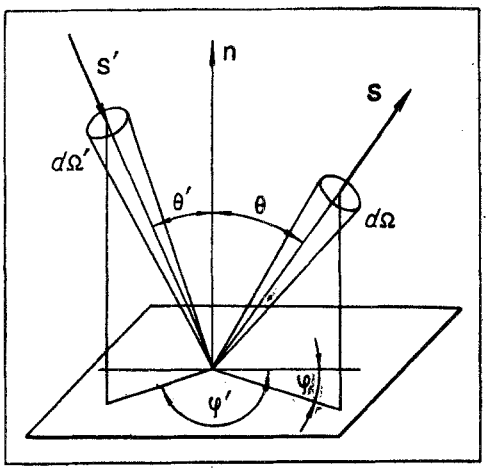

Fig. 3

Fig. 2. Inversion of the temperature dependence of the spectral degree of blackness for tungsten [1) 2800; 2) 2200; 3) 1600°K]. λ, μ.

Fig. 3. Reflection from a surface.

Some rough materials have an interesting feature in the infrared; oblique incidence on a very rough surface results in an indicatrix elongated not in the specular direction but tending towards the direction of incidence.

Toporets [73] found that a specular component of diffraction–interference origin is present at large angles of incidence for a rough surface.

Although there are detailed formulas for $p_\nu(s', s)$ for various technical materials, they do not explain all the observations.

Davis and others [35, 74-78] have examined theoretically the effects of λ and roughness on $p_\nu(s', s)$, e.g., the relative indicatrix is [35, 76]

$$\frac{p_\nu(\theta', 0; \theta, \varphi)}{p_\nu(\theta', 0; -\theta', 0)} = \frac{1}{32\pi^2}\left(\frac{m_r}{a_r}\right)^2 (\cos\theta' + \cos\theta)^2 \exp\left\{-\frac{1}{2}\left(\frac{m_r}{a_r}\right)^2 \left[\frac{(\sin\theta\cos\varphi - \sin\theta')^2 + \sin^2\theta\sin^2\varphi}{(\cos\theta' + \cos\theta)^2}\right]\right\}. \quad (26)$$

Here the topography is represented via the rms slope s_r, which is related to the roughness height a_r and the scale m_r by $m_r/a_r = \sqrt{2}/s_r$, which applies for $a_r/m_r < 1$ and $a_r/\lambda \sim 1$.

Beckman's formula [78] agrees better with experiment; it gives the indicatrix $p_\nu(\theta', \pi; \theta, \varphi)$ as consisting of a coherent or specular component $r_{\nu m}(\theta') \cdot p_m(\delta)$ and a diffuse or nonspecular one $p_{\nu d}(\theta', \pi; \theta, \varphi)$:

$$p_\nu(\theta', \pi; \theta, \varphi) = r_{\nu m}(\theta')\, p_m(\delta) + p_{\nu d}(\theta', \pi; \theta, \varphi). \quad (27)$$

The following are the expressions for the quantities in (27):

$$r_{\nu m}(\theta') = \exp\left\{-\left[4\pi\left(\frac{a_r}{\lambda}\right)\cos\theta'\right]^2\right\};$$

$$p_{\nu d}(\theta', \pi; \theta, \varphi) = \frac{\pi(a_r/\lambda)^2}{\cos\theta'\cos\theta}\left[\frac{1 + \cos\theta\cos\theta' - \sin\theta\sin\theta'\cos\varphi}{\cos\theta + \cos\theta'}\right]^2 \exp\left\{-\left[2\pi\left(\frac{a_r}{\lambda}\right)(\cos\theta + \cos\theta')\right]^2\right\}$$

$$\times \sum_{m=1}^{\infty}\left\{\frac{[4\pi^2(a_r/\lambda)^2(\cos\theta + \cos\theta')^2]^m}{m(m!)}\right\} \exp\left\{-\pi^2\left(\frac{a_r}{\lambda}\right)^2 \frac{[\sin^2\theta' + \sin^2\theta - 2\sin\theta'\sin\theta\cos\varphi]}{m}\right\};$$

$$p_3(\delta) = \frac{\delta(\theta' - \theta)\,\delta[\varphi' - (\varphi + \pi)]}{\cos\theta'\, d\Omega'};$$

$$\delta(x) = \begin{cases} \infty & \text{for } x = 0 \\ 0 & \text{for } x \neq 0 \end{cases}; \qquad \int_{-\infty}^{\infty} \delta(x)\, dx = 1$$

It has been found [35] that the optical roughness a_r is greater than the rms roughness by 40-76%: $a_r \approx 1.40$-$1.76\, h_{rm}$.

These formulas have not yet been thoroughly tested by experiment and do not describe all the features of the reflection.

Also, experimental values for $p_\nu(s', s)$ are known only for a few materials over narrow ranges in λ, T, and angle of incidence.

The following conclusions can be drawn about the state of our knowledge:

1) Many of the theoretical formulas are imperfect; they have only restricted limits of use and do not take into account the real state of the surface.

2) The theoretical relationships require experimental confirmation over wider ranges of temperature, wavelength, and surface state in order to provide for more reliable extrapolation.

3) Much too little is known about the directional spectral characteristics and optical properties of technical materials.

The evidence on primary radiation characteristics is inadequate to allow detailed technical calculations for most technical materials.

3. Mean Radiative Characteristics of Solids. Most existing measurements on radiation parameters relate to average or integral characteristics.

a) Integral characteristics have been examined for most technical materials over fairly wide temperature ranges, since these are the characteristics used in most design calculations on radiative transfer. Although there is abundant experimental evidence on these characteristics, the variety of operating conditions for materials do not yet allow us to make satisfactory theoretical generalizations. Of the theoretical results, the main importance attaches to some formulas derived from the electromagnetic theory, e.g., ones derived [32] for the hemispherical emissivity by averaging $\varepsilon_\nu(s)$ over a hemisphere:

$$\varepsilon_{\nu H} = \frac{1}{\pi}\int_0^{2\pi}\int_0^{\pi/2} \varepsilon_\nu(s)\cos\theta\sin\theta\, d\theta\, d\varphi. \tag{28}$$

The electromagnetic results are used for $\varepsilon_\nu(s)$ in (28) to get $\varepsilon_{\nu H}$ [79]; Fig. 4 shows $\varepsilon_{\nu H}$ as a function of k_ν and n_ν.

Analytic expressions are available [32, 79, 80] for $\varepsilon_{\nu H}$ in certain special cases, e.g., for insulators ($k_\nu = 0$)

$$\varepsilon_{\nu H} = \frac{1}{2} - \frac{(3n_\nu+1)(n_\nu-1)}{6(n_\nu+1)} - \frac{n_\nu^2(n_\nu^2-1)^2}{(n_\nu^2+1)^3}\ln\left(\frac{n_\nu-1}{n_\nu+1}\right) + \frac{2n_\nu^3(n_\nu^2+2n_\nu-1)}{(n_\nu^2+1)(n_\nu^4-1)} - \frac{8n_\nu^4(n_\nu^4+1)}{(n_\nu^2+1)(n_\nu^4-1)}\ln n_\nu. \tag{29}$$

If the material is such that $\sin^2\theta \ll n_\nu^2(1+k_{0\nu}^2)$, we have

$$\varepsilon_{\nu H} = 4n_\nu - 4n_\nu^2\ln\left(\frac{1+2n_\nu+n_\nu^2+n_\nu^2k_{0\nu}^2}{n_\nu^2+n_\nu^2k_{0\nu}^2}\right) + \frac{4n_\nu^2(1-k_{0\nu}^2)}{k_{0\nu}}\operatorname{arctg}\left(\frac{k_{0\nu}}{1+n_\nu+n_\nu k_{0\nu}^2}\right) + \frac{4}{n_\nu(1+k_{0\nu}^2)}$$
$$- \frac{4\ln(1+2n_\nu+n_\nu^2+n_\nu^2k_{0\nu}^2)}{n_\nu^2(1+k_{0\nu}^2)^2} + \frac{4(1+k_{0\nu}^2)}{n_\nu^2k_{0\nu}(1+k_{0\nu}^2)^2}\operatorname{arctg}\left(\frac{n_\nu k_{0\nu}}{1+n_\nu}\right). \tag{30}$$

Drude's theory gives [7, 32, 46, 47, 71, 81] for metals the spectral hemispherical degree of blackness as

$$0<\rho/\lambda<0.5 \quad \varepsilon_{\nu H} = 0.476\sqrt{\rho/\lambda} - 0.148\rho/\lambda,$$
$$0.5<\rho/\lambda<2.5 \quad \varepsilon_{\nu H} = 0.442\sqrt{\rho/\lambda} - 0.0995\rho/\lambda, \tag{31}$$

and the emissivities integrated over the entire spectrum: normal

$$\varepsilon(0) = 0.576\sqrt{\rho T} - 0.124\,\rho T \tag{32}$$

and hemispherical

$$\varepsilon_H = 0.751(\rho T)^{1/2} - 0.632(\rho T) + 0.670(\rho T)^{3/2} - 0.607(\rho T)^2 \tag{33}$$

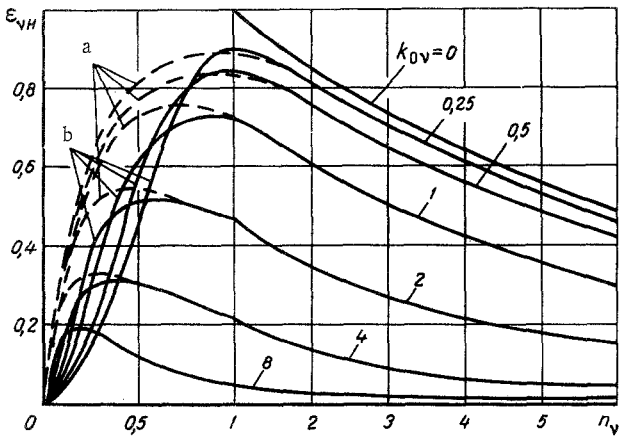

Fig. 4. Hemispherical spectral blackness as a function of the optical parameters: a) from (30); b) by exact calculation.

or

$$0<\rho T<0.2 \quad \varepsilon_H=0.751\sqrt{\rho T}-0.396\,\rho T,$$

$$0.2<\rho T<0.5 \quad \varepsilon_H=0.698\sqrt{\rho T}-0.266\,\rho T.$$

There are [58, 130] also some empirical formulas for the integral degree of blackness:

$$\varepsilon(0)=1-\exp\left(-\frac{c'}{\sqrt{\varkappa}}T\right),$$

$$\varepsilon(0)=1-\exp(-\beta' T).$$

These averaged values relate to smooth surfaces, as do the initial directional quantities. In the main, these formulas reflect correctly the observed T dependence for the integral properties, though they remain restricted in application or contain empirical coefficients.

b) The emission from a real surface of arbitrary shape may be characterized by an effective emissivity if the surface element is much larger than the scale of the roughness and inhomogeneity. Most technical materials have rough surfaces, and some of them have porous coatings, grooves, or ridges designed to increase the emissivity. There are many papers on the effects of roughness on emissivity, and this topic will be considered briefly.

The exact approach to description of the effective emission for a rough surface varies with the ratio of the geometrical size to the wavelength and also with the thermal conductivity (Fig. 5). The emission coefficient is increased if the surface has inclusions and microinhomogeneities smaller than the wavelength (Fig. 5a), which has [82] been ascribed to altered dielectric parameters, for which purpose use was made of Loor's [83] theory of the dielectric parameters of heterogeneous mixtures. Py derived an expression for σ_r (the electrical conductivity of a rough surface) for roughness and pores of cylindrical and elongated shape:

$$\sigma_r=\frac{1-\xi}{1+\xi}\sigma \text{ and } \sigma_r=\left(1-\frac{3}{2}\xi\right)\sigma, \tag{34}$$

where ξ is the volume fraction of the microdispersed phase in the surface layer. Py used this expression to derive the total emissivity of a rough surface via formulas from the electromagnetic theory:

$$\varepsilon_r=\varepsilon_s\left(\frac{1+\xi}{1-\xi}\right)^{1/2} \text{ and } \varepsilon_r=\varepsilon_s\left(1-\frac{3}{2}\xi\right)^{-1/2}. \tag{35}$$

It has been confirmed by experiment [82] that ε_r (for a microrough surface) is proportional to ε_s (for a smooth one).

There is (Fig. 5b) another mechanism that increases the effective ε when the roughness has a scale greater than the wavelength. The effective emission is increased because the emission from the surface itself is supplemented by radiation from other elements reflected from the surface. The general result for an isothermal surface is

$$\varepsilon_{\nu e}(N)=\varepsilon_\nu(N)+[1-\varepsilon_\nu(N)]\int_{F_r}\varepsilon_{\nu e}(P)K(N,P)\,dF_p. \tag{36}$$

It has been assumed that $p_\nu=1$ (diffusing surface). This equation or an analogous one has been used in calculations on the emission from cavities of various shapes with isothermal walls and also for several nonisothermal cases [33, 84-87].

Simplified formulas have been proposed for the $\varepsilon_{\nu e}$ of rough surfaces, e.g., if the surface of a cavity is isothermal, opaque, and absorbs and emits diffusely, the result is

$$\varepsilon_r=\frac{\varepsilon_s}{\varepsilon_s+(1-\varepsilon_s)F}, \tag{37}$$

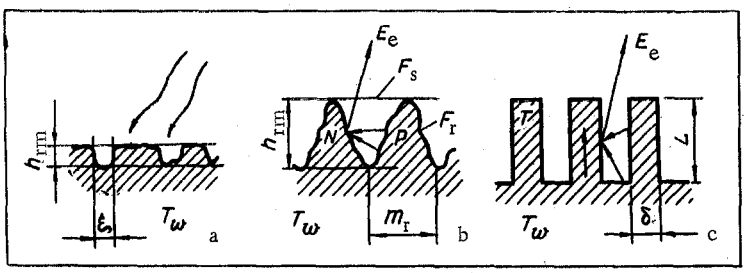

Fig. 5. Scheme of real surface radiation for various types of surface roughness: a) $\lambda > h_{rm}$; b) $\lambda < h_{rm}$; T_w = inv; c) $\lambda \ll h_{rm}$, T_w = var.

where F is the mean inclination of the cavity relative to the exit aperture (the roughness factor [88]), which for equal-sided surfaces is approximately equal to the ratio of F_s (area of the geometrical enclosing surface) to F_r (total surface area).

Agababov has examined roughness factors for cavities of various shapes and has made measurements that confirm that (37) can be used for the degree of blackness for surfaces with various types of roughness.

It is difficult to determine F_r for a real surface, so one often uses characteristics of the surface finish such as h_{rm} (the rms roughness height) or h_{rm}/m_r (the ratio of this to the mean distance between roughness peaks) [89, 90, 92, 93]. However, these quantities do not determine the optical roughness unambiguously [90], e.g., one does not obtain a single curve on plotting ε against h_{rm}.

If the roughness cavities are not isothermal (Fig. 5c), one has to incorporate thermal conduction in the solid in calculating $\varepsilon_{\nu e}$. An analogous problem arises in considering a ribbed surface, which is of considerable practical importance in space research, and there are many papers on the topic [95, 96]. Here $\varepsilon_{\nu e}$ is dependent not only on the degree of blackness and the shape of the roughness or ridges but also on the radiation–conduction transport number $N = \varepsilon_s \sigma_0 T_w^3 L^2/\varkappa\delta$ (Fig. 5c), i.e.,

$$\varepsilon_e = \varepsilon_e(\varepsilon_s;\ F_s/F_r\ ;\ N). \tag{38}$$

c) Effects of surface structure. Polishing not only alters the form of the surface but sometimes also alters the state of the surface layer [98-103], e.g., a material with an oriented structure such as pyrographite [99, 103] becomes amorphous on polishing, which increases the degree of blackness.

The structure is also affected by annealing, degassing, and selective loss of atoms on heating to high T; for instance, the surface of a single crystal may become smoother on heating, while a polycrystalline material becomes rougher.

There have been some measurements on the effects of surface structure, crystal orientation, etc., on emissivity, but we do not yet have any quantitative relation of emissivity to structure.

d) Effective emission from a semitransparent body. The effective emissivity of a semitransparent body is an important practical characteristic. A body is considered as semitransparent if k_ν is small, i.e., the radiation penetration depth

$$L_\nu = \frac{1}{\alpha_\nu} = \frac{\lambda}{4\pi k_\nu}$$

is comparable with the thickness within which there is an appreciable temperature change [108]. Most insulators fall in this class, and the effective emissivity is dependent not only on the above characteristics but also on the temperature distribution in the body, which is governed by the direction and magnitude of the heat fluxes carried by conduction and radiation, i.e., $\varepsilon_e = \varepsilon_e[\varepsilon(n_\nu, k_\nu); \varepsilon\sigma_0 T^3 x/\varkappa]$.

There are several papers on heat transport in a plane-parallel layer, e.g., numerical solutions [105, 106] for an absorbing medium, sometimes [107] with allowance for scattering. One paper [104] discusses emission under these conditions. All of these papers give only approximate solutions because it is difficult to solve exactly the integrodifferential equations for the process. Also, it is always assumed that the body is gray and a diffuser (directional and selective features are neglected). There are only two papers [109, 110] on the problem for bodies that are not gray.

The emissivity of a semitransparent body is a functional, i.e., is dependent on the detailed transfer conditions, so the following requirements have to be met in order to determine the emissivity: 1) a detailed study has been made of the primary radiation characteristics; 2) a reasonably complete solution is available for the transport by conduction and radiation in real bodies.

Entirely analogous problems arise for the properties of the layered materials frequently used in space research and so on. We cannot enter here into the attempts to solve this problem for particular cases and merely note that there are several papers on the topic [101, 102, 111-114].

4. Radiative Parameters of Solids Used in Heat-Transfer Calculations. Parameters of the accuracy appropriate to the accuracy of the calculations must be used in relation to radiative heat transfer. We examine this by reference to the radiative transfer between two parallel plates. In the gray approximation, the resultant flux takes the form

$$E_{p12}=\frac{\sigma_0(T_1^4-T_2^4)}{\frac{1}{\varepsilon_1}+\frac{1}{\varepsilon_2}-1}. \tag{38}$$

Here we use the integral hemispherical emissivities of the two bodies, which are taken as equal to the absorptivities and as independent of direction. This approach is adequate for estimates, but most bodies are not gray emitters, and for these one has to distinguish between the integral emissivity ε and the integral absorptivity a, which are not the same because the bodies are not gray and diffusing. The resultant flux is then calculated from

$$E_{p12}=\frac{\sigma_0\left(\frac{\varepsilon_1}{a_1}T_1^4-\frac{\varepsilon_2}{a_2}T_2^4\right)}{\frac{1}{a_1}+\frac{1}{a_2}-1}, \tag{39}$$

in which ε is the integral hemispherical emissivity and a is the integral hemispherical absorptivity. The first of these is dependent on T and the properties of the body and is a functional because it is dependent on the spectral composition of the incident flux, so it cannot be determined accurately in advance. Various simplifications are therefore used to estimate a, and the applicability of these has to be tested in each particular instance.

For instance, a for a metal surface is taken [115] as equal to ε for the geometric-mean temperature $T=\sqrt{T_1T_2}$, which is correct if the temperature dependence of the spectral properties is in accordance with the electromagnetic theory and if black-body radiation of temperature T_2 is incident on the metal; but we have seen that the electromagnetic theory does not describe the emissivity in the visible and near-infrared regions, so this method can produce errors at high T.

The following integral absorptivity gives good results in approximate calculations for metals and nonmetals:

$$a_1(T_1,\ T_2)=\frac{\int_0^\infty \varepsilon_{\nu 1}(T_1)E_{0\nu}(T_2)\,d\nu}{\int_0^\infty E_{0\nu}(T_2)\,d\nu}. \tag{40}$$

Such calculations have [117] been performed for real technical surfaces (steel) showing selectivity: unoxidized, oxidized, and ash-coated. Relationships approximating to (40) were derived for these.

The following formula is used to determine exactly the radiative transfer between two selectively and diffusely emitting plates:

$$E_{p12}=\int_0^\infty \frac{E_{0\nu}(T_1)-E_{0\nu}(T_2)}{\frac{1}{\varepsilon_{\nu 1}}+\frac{1}{\varepsilon_{\nu 2}}-1}\,d\nu. \tag{41}$$

This formula can be used if the spectral characteristics are known.

It has been shown that errors of 20-30% can arise if one neglects the selectivity in calculating E_{r12} for metals [35, 61, 118, 119] and, in particular, for clean and dirty steel surfaces [117].

The following formula is used for two bodies with allowance for wavelength and direction effects:

$$E_{p12} = \int_0^\infty \int_{+2\pi} I_{ev}(s) \cos(\hat{sn})\, d\Omega - \int_0^\infty \int_{-2\pi} I_{nv}(s) \cos(\hat{sn})\, d\Omega,$$

$$I_{ev}(s) = \varepsilon_v(s)\, n_v^2 \frac{E_{0v}}{\pi} + \frac{1}{\pi} \int_{+2\pi} I_{nv}(s') \cos(\hat{s'n}) r_v(s')\, p_v(s', s)\, d\Omega. \quad (42)$$

Here one needs to know the reflection indicatrix as well as the emission and absorption spectra. The problem has been considered for two intersecting planes [120] and for two parallel plates [77, 121]; it has been shown that large errors can arise (local intensity errors up to factors of 3) if the directional effects are neglected. However, there is not much change in the mean fluxes if one neglects directional effects.

This calculation is too tedious to use in engineering design; also, we lack data on the primary spectral and directional characteristics for technical materials.

It is sufficient to know integral radiative characteristics for the purpose of approximate heat-transfer calculation. More accurate calculations require detailed knowledge of the emission and absorption characteristics.

5. Measurement of Radiative Characteristics of Solids. The measurement methods have to be chosen in accordance with the methods of design calculation, especially where integral characteristics are concerned. The latter are and will be especially important for engineering calculations on technical materials.

Heating methods (electron-beam heating, induction heating, resistive heating, solar furnaces, etc.) enable one to reproduce various radiative heat-transfer conditions as regards spectrum and directional distribution. These techniques enable one to derive the integral characteristics directly, and they have been adequately tested in a number of apparatuses [100, 113, 114, 123-127, 129], which have been used with numerous materials in various surface states over wide temperature ranges.

On the other hand, little work has been done on apparatus and measurement methods for primary spectral and directional characteristics of technical materials. Some methods have recently been developed, and preliminary evidence has been obtained, mainly on the normal spectral degree of blackness for heat-resisting materials [11, 56, 63, 65, 99] and on the spectral reflectivity at room temperature. Less is known about the spectral directional characteristics and optical parameters of technical materials [63, 72, 99].

Primary radiation characteristics for technical materials provide a basis for more accurate radiative-transfer calculations for technical processes and also provide a way of checking theoretical principles. These characteristics also enable one to monitor the structure and physical properties of materials in technical processes.

There are more detailed surveys [35, 52, 53, 100, 125, 127, 131] of the various methods of examining radiative properties of solids, and also of the results.

NOTATION

I is the radiation intensity;
E_e is the effective radiation flux;
E_i is the incident flux;
E_{ref} is the reflected flux;
E_r is the resultant flux;
$E_{0\nu}$ is the spectral density of black-body flux;
q is the radiation flux vector;
u is the radiation energy density;
D is the electric induction vector;
B is the magnetic induction vector;

$\mathbf{E}$ is the electric field vector;
$\mathbf{H}$ is the magnetic field vector;
$\mathbf{j}$ is the electric current vector;
f is the charge concentration;
T is the temperature;
t is the time;
ε_d is the dielectric constant;
μ is the magnetic permeability;
σ is the optical conductivity;
σ_s is the static electrical conductivity;
ρ is the specific resistance;
$\varkappa$ is the thermal conductivity;
N is the radiative–conductive transport number;
c_0 is the speed of light in vacuum;
c_ν is the monochromatic speed in medium;
c is the mean speed in medium;
n_ν is the refractive index;
k_ν is the absorption index;
α'_ν is the effective spectral absorption coefficient;
α_ν is the spectral absorption coefficient;
α'_{me} is the mean radiation coefficient;
α' is the mean absorption coefficient;
β_ν is the scattering coefficient;
γ_ν is the scattering indicatrix;
p_ν is the reflection indicatrix;
p_{ba} is the bidirectional reflectivity;
ε is the emissivity;
r is the reflectivity;
a is the absorptivity;
τ is the transmission;
ν is the frequency;
λ is the wavelength;
ω is the circular frequency;
ν_p is the plasma frequency;
ω_i is the circular frequency of free vibrations of electrons;
γ is the oscillation decrement;
L_ν is the mean free path for radiation;
$\mathbf{s}'$ is the direction of incident ray;
$\mathbf{s}$ is the direction of reflected ray;
φ is the azimuthal angle;
θ is the polar angle;
Ω is the solid angle;
ξ is the proportion by volume of dispersed phase;
F is the roughness factor;
F_s is the equivalent smooth surface area;
F_r is the actual rough surface area;
h_{rm} is the root-mean-square roughness height;
a_r is the optical roughness height;
s_r is the root-mean-square inclination of roughness;
m_r is the mean distance between roughness ridges;
N_e is the electron concentration;
e is the electronic charge;
m is the effective electron mass;
k is the Boltzmann's constant;
h is the Planck's constant;
σ_0 is the Stefan's constant.

Subscripts

ν denotes the monochromatic;
e denotes the effective;
i denotes the incident;
p denotes the resultant;
s denotes the smooth;
r denotes the rough;
m denotes the mirror.

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