OPTICAL ANISOTROPY OF METALLIC TEXTURES

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Abstract

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OPTICAL ANISOTROPY OF METALLIC TEXTURES

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Recently, polycrystalline textures imitating the anisotropic properties of single crystals have acquired increasing importance. Textures are systems consisting of an aggregate of microcrystals oriented in a definite manner. Among them, in particular, are optical textures, which may possess birefringence, rotation of the plane of polarization, and dichroism. The dichroism of textures is caused either by the intrinsic dichroism of oriented particles, or by the shape and ordered arrangement of optically anisotropic particles ([1–3]).

Fig. 1. Absorption curves of textures of two types

In the present work, metallic dichroic textures have been produced and a connection has been established between their structure and optical properties. The textures obtained consist of anisometric metallic microcrystals located in oriented high-polymer films and possess clearly pronounced dichroism. Thus, textures of gold microcrystals show strong dichroism in the visible (Fig. 1*a*) and near-infrared (Fig. 1*b*) regions of the spectrum, which makes it possible to use them as infrared polarizers. It is possible to obtain a series of textures with intermediate properties, as well as textures that polarize the longer-wavelength part of the infrared spectrum.

The optical properties of colloidal metals have been explained on the basis of the theory of radiation scattering developed by Mie ([4]) for spherical particles of arbitrary sizes. Gans ([5]) considered radiation scattering by ellipsoidal particles infinitely small in comparison with the wavelength. In both cases, radiation scattering by anisometric particles of finite dimensions is not considered.*

* In work ([6]), the influence of both size and degree of anisometry on radiation scattering is taken into account simultaneously; however, no formulas applicable to the corresponding calculations are given.

Fig. 2. Absorption curves calculated for gold particles: a—by Mie formulas; b—by Gans formulas for elongated ellipsoids with axial ratio A/B = 1 (1); 1.75 (2); 2.5 (3); 5 (4); 7 (5); 10 (6); ∞ (7). All values $K_\perp$ lie in the hatched region.

Figure 2: Fig. 2. Absorption curves calculated for gold particles: a—by Mie formulas; b—by Gans formulas for elongated ellipsoids with axial ratio A/B = 1 (1); 1.75 (2); 2.5 (3); 5 (4); 7 (5); 10 (6); ∞ (7). All values $K_\perp$ lie in the hatched region.

In the present work, the Mie and Gans methods are applied to explain the optical properties of anisotropic colloidal media. The influence of the sizes of colloidal gold particles on the optical properties of textures was investigated by the Mie method. The anisometry of the particles was taken into account in two ways: first, according to Gans, without taking account of particle sizes; second, by representing one finite anisometric particle in the form of two spherical particles, with subsequent calculation by Mie. A particle of elongated shape was replaced in the calculations in one case by a sphere whose diameter was taken equal to the length of the particle, and in the other by a smaller sphere with a diameter equal to the width of the particle. In passing from one particle to the texture as a whole, it is essential that all particles in the texture are oriented and that the incident radiation is polarized. The calculation was therefore carried out for two perpendicular directions: along and across the axis of orientation of the particles. Such an approach is a certain approximation, but nevertheless it makes it possible to explain the optical properties of the textures and to obtain some quantitative estimates.

According to Mie formulas (7), values were calculated for the coefficients of total absorption (absorption + scattering) (Fig. 2a) for gold particles with diameters of 400, 600, 1000, 1400, 1800, and 2400 Å, placed in a binding medium—polyvinyl alcohol, whose refractive index is 1.519. The calculations were carried out for the spectral range 400–1400 mμ, where absorption by the binding medium is practically absent. The optical constants of gold were taken from works (8, 9). Depending on the ratio of the particle radius a to the wavelength λ ($x = 2\pi a/\lambda$), from one ($x < 0.8$) to four ($x > 1.6$) partial waves were taken into account in the calculations. The relative error in this case did not exceed 2%. The coefficients of total absorption were calculated for a volume concentration of gold of 10^{-6}.

Fig. 2. Absorption curves calculated for gold particles: **a**—by the Mie formulas: 1—diameter $2a \ll \lambda$; 2—$2a = 600$ Å, 3—1000 Å, 4—1400 Å, 5—1800 Å, 6—2400 Å; **b**—by the Gans formulas for elongated ellipsoids with axial ratio $A/B = 1$ (1); 1.75 (2); 2.5 (3); 5 (4); 7 (5); 10 (6); ∞ (7). All values of $K_\perp$ lie in the hatched region.

The calculated curves show that large particles possess greater absorption in the near infrared region of the spectrum, whereas in the visible region, conversely, the smallest particles do. Precisely this dependence is observed experimentally: from the experimental curves (Fig. 1b) it is seen that absorption along the axis of the elongated particles, corresponding in the calculations to the larger radius, in the infrared region considerably exceeds ···

absorption in the transverse direction. Comparing the positions of the absorption maxima of the experimental and calculated curves, one can in each individual case estimate the particle size. Thus, comparison of the absorption curves shown in Fig. 1a with the calculated curves (Fig. 2a) gives a particle size in the longitudinal direction of 500–600 Å, and in the transverse direction—much less than the wavelength. For dichroism to appear in the near infrared region, the particle length must be no less than 2000 Å, with a transverse size not exceeding 200–400 Å. The particle size in textures of an intermediate type can be estimated analogously. Thus, the calculated curves of total absorption for gold particles of various sizes make it possible to explain the appearance of dichroism in the visible and near infrared regions of the spectrum, and to estimate the particle sizes and the degree of their anisometricity.

It is interesting to compare the particle sizes obtained from optical data with the results of electron microscopy. Electron-microscopic images of texture specimens obtained by the ultrathin-section method show the presence in the textures of individual elongated gold particles oriented in one direction (Fig. 3). The particle sizes determined from the electron-microscopic images ($\sim$ 1000 Å) agree quite well with those calculated from the optical data ($\sim$ 1200 Å) (see inset, p. 548).

To clarify the influence of the degree of anisometricity on the polarizing properties of the textures, calculations were made of the total absorption coefficients for ellipsoidal gold particles whose dimensions are much smaller than the wavelength. In contrast to Gans, who considered a system of unoriented particles, the calculation was carried out for oriented ellipsoids of revolution, similarly to how this was done in Cherdyntsev' s work [10]. Elongated ellipsoids of revolution were considered with the following ratios of semiaxes: 1; 1.3; 1.75; 2.1; 2.5; 5; 7; 10; ∞. The calculations were performed for the region 400–1400 mμ using the same optical constants and the same volume concentration of gold. The results of the calculations show that when the particles are oriented, the absorption maximum corresponding to unoriented particles is split. The absorption maximum along the elongated axis of the ellipsoid, $K_{\parallel}$, is shifted into the long-wavelength region, while the absorption maximum along the smaller axis of the ellipsoid, $K_{\perp}$, is shifted into the short-wavelength region. In this case the shift of the maximum $K_{\perp}$ is very small, whereas the maximum $K_{\parallel}$ is displaced strongly into the long-wavelength region, broadening and increasing in intensity as the degree of anisometricity increases. In Fig. 2b the values of $K_{\parallel}$ and $K_{\perp}$, calculated for ellipsoids with different ratios of semiaxes, are given.

Thus, metallic textures possessing strong polarizing properties in the near infrared region of the spectrum have been obtained for the first time, and an interpretation of the dichroism of these textures has been given within the framework of scattering theory. The results of the calculations are of general significance for the optics of anisotropic colloidal systems.

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