

this seems to be the case in the history of physics. Any basic work of physical importance ultimately finds practical applications.

We conclude by emphasizing that optical spectroscopy has finally grown to become a part of the new rapidly expanding technology, and we hope our tradition in optics established by Professor C. V. Raman would play a leading role in developing opto-electronics in India.

1. Bhagavantam, S., *Ind. Jour. Phys.*, 1930, 5, 169.
2. Bloembergen, N., *Am. Jour. Phys.*, 1967, 35, 989.
3. Dumke, W. P., *Phys. Rev.*, 1962, 127, 1559.
4. Javan, A., Bennet, W. B., Jr. and Herriott, D. H., *Phys. Rev. Letters*, 1961, 6, 106.
5. Jha, S. S., In *Solid State Physics*, edited by F. C. Auluck, Thomson Press, New Delhi, 1971, 2.
6. Kastler, A., *Proc. Phys. Soc.*, 1954, 17 A, 853.
7. Krishnan, R. S., *Nature*, 1947, 160, 26.
8. Maiman, T. H., *Ibid.*, 1960, 187, 493.
9. Mani, A., *Proc. Ind. Acad. Sci.*, 1942, 15, 52.
10. Narayanan, P. S., *Ibid.*, 1948, 28, 469.

11. Nayar, P. G. N., *Proc. Ind. Acad. Sci.*, 1942, 15, 310.
12. Patel, C. K. N., *Phys. Rev.*, 1964, 136, A 1187.
13. — and Shaw, F. D., *Phys. Rev. Letters*, 1970, 25, 8.
14. Prokhorov, A. M., *Jour. Expt. Theor. Phys. USSR*, 1958, 34, 1658.
15. Raman, C. V., *Phil. Mag.*, 1915, 30, 70.
16. —, *The Physiology of Vision*, The Indian Academy of Sciences, Bangalore, 1968.
17. — and Krishnan, K. S., *Phil. Mag.*, 1928, 5, 498.
18. — and Nagendra Nath, N. S., *Proc. Ind. Acad. Sci.*, 1936, 3, 75; *Ibid.*, 1936, 3, 119.
19. Ramanathan, K. R., *Physics News*, 1970, 1, 36.
20. Ramaseshan, S., *Proc. Ind. Acad. Sci.*, 1948, 28, 360.
21. Schawlow, A. L. and Townes, C. H., *Phys. Rev.*, 1958, 112, 1940.
22. Sirkar, S. C. and Chakravarty, D., *Ind. Jour. Phys.*, 1935, 9, 553.
23. Sorokin, P. P. and Lankard, J. R., *IBM Jour. Res. Devel.*, 1966, 10, 162.
24. Venkateswaran, C. S., *Proc. Ind. Acad. Sci.*, 1935, 5, 459.
25. —, *Ibid.*, 1936, 3, 25.
26. Thosar, B. V., *Phil. Mag.*, 1938, 26, 580; *Ibid.*, 1938, 26, 878.
27. —, *Jour. Chem. Phys.*, 1944, 12, 424.
28. Yarborough, J. M., Sussman, S. S., Puthoff, H. E., Pantell, R. H. and Johnson, B. C., *Appl. Phys. Letters*, 1969, 15, 102.

COLOURS OF THIN BLACK NICKEL DEPOSITS*

S. R. RAJAGOPALAN

Materials Science Division, National Aeronautical Laboratory, Bangalore-17

1. INTRODUCTION

BRIGHT lustrous metallic coatings of immense decorative appeal generally result from electroplating. But there are instances where coloured deposits are formed by deposition. Black nickel—obtained by the electrolysis of a solution containing nickel sulphate, zinc sulphate and ammonium thiocyanate—is one such example. Poor (1943) noticed that these deposits exhibited vivid colours in thin layers and were black in thick layers. He attributed the colours of black nickel to be due to interference in thin films. This hypothesis appears, at the outset, to be incongruent with some of the salient

features of black nickel that emerged from our studies. Prof. C. V. Raman's work on the colours of many materials considerably influenced us and paved the way for understanding the phenomenon of colours of black nickel. I shall endeavour now to discuss this in some detail.

2. EXPERIMENTAL OBSERVATIONS ON BLACK NICKEL

The deposits are definitely metallic as they evolved hydrogen on being reacted with acids. They show appreciable electronic conductivity. The colour changes sequentially, i.e., in the order yellow, red, blue, green, yellow, etc., with thickness which is reminiscent of interference phenomenon.

* Talk delivered at the 37th Annual Meeting of the Indian Academy of Sciences.

For interference effects it is necessary that films should be transparent at least to a certain degree and would therefore be absent at such thicknesses where the transmitted intensity would be less than 1%. A calculation shows that the transmitted intensity would be less than 1% at a thickness of 464 and 635 Å respectively for zinc and nickel films. Black nickel deposit contains nickel and zinc. Therefore it is to be expected that in deposits thicker than 600 Å, the interference effect should be negligible. Experimentally we find that saturated colours could be observed in black nickel upto a thickness of 3000 Å.

Another interesting feature of thin black nickel is that the colour of the deposit shifts significantly to the blue end of the spectrum when it is immersed in a liquid of higher refractive index; for instance, an yellow-orange deposit on immersion in benzyl alcohol ($n = 1.54$) would appear green. After removing the deposit from the liquid and drying, it again appears yellow-orange.

The observations described above indicate that the origin of colours of black nickel poses a problem because of the following interesting features:

- (a) The film is metallic and yet shows colours up to 3000 Å.
- (b) The colours change regularly with thickness.
- (c) The colour shifts significantly to the shorter wavelength when the refractive index of the surrounding medium is increased.

3. PROF. RAMAN'S WORK ON COLOURS ARISING FROM OPTICAL PHENOMENA

Colours arise in nature either due to absorption or due to optical phenomena. Prof. Raman has investigated most extensively the colours arising due to different optical phenomena. We investi-

gated whether the colours of black nickel could be due to any one of them.

Prof. Raman was interested in scattering and diffraction of light by metallic films. In Professor's laboratory at Calcutta, Ramdas (1925-26) investigated the scattering properties of vacuum evaporated films and found that these films did not show surface scattering unlike mercury which exhibits surface scattering due to thermal roughening (Raman and Ramdas, 1925). Ramaswamy (1934, 1937) pursued the work of Ramdas, and found that very thin silver films (thickness less than 100 Å) showed bright colours in reflection, transmission and scattering. The reflected and transmitted colours were approximately complementary whereas the scattered colour did not show any such relation to the transmitted or reflected colour. These films were found to have resistances from a few hundred ohms to almost infinity. From the electrical conductivity measurement they concluded that the film is not coherent but consisted of a random distribution of particles. Many years later Sennett and Scott (1950) proved by electron microscopy that very thin metal films are not coherent. Experiments with black nickel, coated on conducting glass substrate, did not reveal any scattering thereby showing that the colours of these deposits are not similar to those observed by Ramaswamy (1934, 1937).

Prof. Raman (1953) showed that in the case of opals the colours are due to stratified media. When a medium is made up of a succession of alternate strata of two different substances having thicknesses d_1 and d_2 and refractive indices n_1 and n_2 , the reflections from successive boundaries could have complete agreement of their phases for a particular wavelength, and hence we could get a

monochromatic reflection. An elegant mathematical theory of the phenomenon has been developed by G. N. Ramachandran (1942). The diagnostic criterion for colours due to stratified medium is, for a given interlamellar spacing the reflection colour is fixed.

Many electrodeposits show laminar growth. We thought that black nickel might also show such a characteristic, since the growth velocity is smaller in the direction of flow of current compared to that in the perpendicular direction. We tried to look for stratification in black nickel by examining a cross-section and a taper section. For this purpose we used the elegant technique of observing in dark ground illumination with oblique incidence described by Prof. Raman (1940). We could not see any stratification. Hence we concluded that the colours of black nickel are not due to reflection from stratified medium. The fact that the colour of the deposit depends on thickness of the film cannot be explained by such a phenomenon unless the interlamellar spacing varies with thickness which is very unlikely.

The iridescence of shells provides another interesting optical phenomenon. Prof. Raman (1935) showed that nacre or mother-of-pearl—the innermost layer of numerous molluscan species—consists of discrete crystallites of aragonite imbedded in a cementing network of conchyo-lin and arranged in a series of equidistant layers. These layers meet the surface at a small angle making the surface grooved. As a consequence, the surface of the material gives rise to diffraction spectra accompanying the reflected light. Simultaneously, the stratifications, since they are regularly spaced, yield selective monochromatic reflection. Since both effects have their origin in the same incident beam, they are necessarily

coherent, and he showed that the internal reflection emerges in a direction coinciding with one of the orders of the diffraction spectra, of the same wavelength produced by the surface of the shell.

Such reflection-diffraction spectra are characterised by three features :

- (a) The colour of the spectrum depends on the angle of incidence.
- (b) The direction of the reflection spectrum is different from that of the specularly reflected ray.
- (c) The reflectance spectrum should show a number of orders.

Using a spectrometer fitted with a photocell at the viewing arm the black nickel deposits were examined. The reflectance spectrum did not exhibit any of the above characteristics.

Prof. Raman and Rajagopalan (1939, 1940) while examining the colours of old decomposed glasses found that immersion in liquid changed their colour. They established that old decomposed glass consists of laminations and the colour is due to selective reflections from such laminar structure. The colour change observed on immersing a flake in a liquid was explained by them as due to the penetration of liquid into the rather open structure of lamellae. If such lamellae are present in black nickel then we should see interference fringes due to intruding air film at some spot or other. Since such fringes are absent in black nickel, we do not have an effect similar to the colours of old glass.

4. ORIGIN OF COLOURS OF BLACK NICKEL

Prof. Raman's work established that besides absorption, colours in nature are due to optical phenomena like, scattering, diffraction, selective reflection from stratified media, laminar diffraction and interference. By decisive experiments, we had ruled out all excepting the last

mentioned one, *viz.*, interference as being responsible for the colours of black nickel. Sherlock Holmes remarked to Dr. Watson "If you have eliminated all the possibilities excepting one, then the remaining one is the answer however improbable it might appear to be". We stuck to this and examined rather seriously the possibility that colours of black nickel could arise from an interference phenomenon.

For the manifestation of interference effects the film should be transparent to a certain degree. The metallic nature of black nickel makes one doubt whether they could be transparent upto 3000 Å. To find this out we used an indirect method. A polished polycrystalline cadmium metal shows a marked grain contrast when examined in a polarising microscope. This is due to the optical anisotropy of cadmium which being hexagonal is an optically uniaxial crystal. Black nickel film was deposited on electropolished cadmium and examined in a polarising microscope. The marked grain contrast was still observed! As the thickness of the film was increased, the grain contrast though dull was still visible at a thickness of 3000 Å and the pattern was completely obliterated by a film of 4500 Å, thus establishing that black nickel deposits are transparent even at thicknesses of the order of 3000 Å. Taking that at a thickness of 4000 Å the intensity transmitted by the film is less than 1% of the incident value, the extinction coefficient (*i.e.*, k of the complex refractive index $n-ik$) was estimated and the value turned out to be 0.23. By measuring the state of polarisation of a polarised light pencil after reflection—*i.e.*, by the technique which is now well known by the name ellipsometry—the optical constants n and k of black nickel were found to be $n = 1.76$ and $k = 0.305$.

Though the technique is now fairly widely used for studying thin films and adsorption, Prof. Raman's ideas in this field seem to be very much earlier. For instance, I understand from Dr. S. Ramaseshan that Prof. Raman was always interested in employing the Jamin effect for studying the adsorbed film formed on a clean vacuum cleaved diamond face by exposing it to a gas or vapour.

The estimated and measured values of k are in fair agreement. It is readily seen that the appreciable transparency of black nickel is due to its low value of k . This, however, raises a very interesting question, why should a metallic deposit have such a low value of k ? This problem will be considered a little later.

Since black nickel belongs to the class of films which might be considered to be weakly absorbing, the colours—if they are due to interference—should exhibit the characteristics of interference colours arising in thin, weakly absorbing films on absorbing substrates. A very detailed review on interference colours by Hiroshi Kobota (1940) has been published in the first volume of "Progress in Optics" edited by Wolf. The review covers about 56 references. No mention is made in this article about interference colours due to weakly absorbing films. We therefore examined the characteristic features of such a system. A reflection interference colour arises because of the fact that the phases of the ray reflected at the air film interface and that transmitted and reflected at the film/substrate interface are in complete agreement for a particular wavelength. In the case of a non-absorbing film on a non-absorbing substrate the phase change due to reflection at both interface is π and hence the phase difference between reflected and transmitted ray is only due to the path

difference. If the substrate is absorbing then we have to take into account the reflection phase change (ϕ_2) at film/substrate interface which is in general not equal to π . When the film is weakly absorbing and the substrate strongly absorbing, the ray reflected from air/film interface suffers a phase change of ϕ_1 . The transmitted ray suffers a phase change of ϕ_2 in addition to that due to path difference. So the phase difference between the reflected and transmitted pencils is made up of two portions one due to film thickness (t) and the other due to $\phi_1 - \phi_2$. So the condition for constructive interference for normal incidence is

$$\frac{\lambda(\phi_1 - \phi_2)}{2\pi} + 2n_1 t = m\lambda.$$

The effect of refractive index of the surrounding medium n_0 can now be readily seen. The phase change ϕ_1 increases with n_0 . Therefore, at a particular t , increasing n_0 leads to a decrease in the value of $(\phi_1 - \phi_2)$. Consequently the reflected interference colour should shift to lower wavelength. From the above analysis it can be seen that the unique feature of interference colours due to weakly absorbing films on a metallic substrate is that it depends on the refractive index of the surrounding medium even when the angle of incidence is normal. If this is true it should be possible to measure changes in ϕ_1 by changing n_0 and measuring λ_{max} . To verify this, reflectivity of black nickel films was measured as a function of thickness with air and benzyl alcohol as surrounding media. The experimental value for the change in ϕ_1 due to change in n_0 from 1 to 1.54 is 38.6° . The value calculated from the optical constants of black nickel is 33.6° . The agreement is quite good.

Thus it is seen that the salient features of the colours of black nickel, viz., the sequential variation of colour with thickness, their saturated nature, the change of colour on immersion in liquid could all be understood in terms of interference in thin weakly absorbing films. However the low value of k and metallic nature, i.e., good electronic conduction appear to be incongruent.

To gain an insight into this problem, we determined the composition by chemical analysis and electron diffraction (Indira et al., 1964). These investigations showed that the deposit is a composite of zinc metal (36.6%), zinc sulphide (27.4%) and Ni_3S_2 (30%). The volume fraction of the metal is about 0.3. Further we infer that zinc metal is present as particles of diameter 100 Å or less. So black nickel is actually a composite of metal dispersed in a dielectric matrix.

Maxwell Garnett (1904, 1906) showed by theoretical arguments that the effective optical constant \hat{n}_e of a composite, could be obtained from that of the matrix (n_m) and dispersed phase (\hat{n}_d), if the particle size of the dispersed phase is very much smaller than λ , by the relation

$$\frac{\hat{n}_e^2 - n_m^2}{\hat{n}_e^2 + 2n_m^2} = q \frac{\hat{n}_d^2 - n_m^2}{\hat{n}_d^2 + 2n_m^2}.$$

A consequence of this relation is that when the volume fraction (q) is less than 0.6, a low value of k_e could be got even when the dispersed phase is a metal. We find that the above relation describes in a semiquantitative fashion the optical constants of black nickel.

Low specific resistance of black nickel (of the order of milliohm cm) could also be understood qualitatively in terms of metal plus dielectric composite. However, it is quite probable that the sulphides

which constitute the matrix of black nickel are defect solid state semi-conductors.

1. Poor, J. G., *Metal Finish.*, 1943, 41, 694.
2. Ramdas, L. A., *Proc. Ind. Assoc. Sci.*, 1925-26, 9, 129, 323.
3. Raman, C. V. and Ramdas, L. A., *Proc. Roy. Soc.*, 1925, 1084, 561.
4. Ramaswamy, S., *Proc. Ind. Acad. Sci.*, 1934, 1A, 347.
5. —, *Ibid.*, 1937, 4A, 656.
6. Sennett, B. S. and Scott, G. D., *J. Opt. Soc. Amer.*, 1950, 40, 203.
7. Raman, C. V., *Curr. Sci.*, 1953, 22.
8. Ramachandran, G. N., *Proc. Ind. Acad. Sci.*, 1942, 16A, 336.
9. Raman, C. V. and Rajagopalan, V. S., *Ibid.*, 1940, 11, 469.
10. —, *Ibid.*, 1935, 1A, 567, 574, 859.
11. — and Rajagopalan, V. S., *Ibid.*, 1939, 9, 371.
12. Hineshi Kubota, In *Progress in Optics*, Vol. I, Ed. by Welf, North Holland Pub. Co., Amsterdam, 1940, p. 213.
13. Indira, K. S., Rajagopalan, S. R., Siddiqi, M. I. A. and Doss, K. S. G., *Electrochim. Acta*, 1964, 9, 1301.
14. Maxwell Garnett, J. C., *Phil. Trans. Roy. Soc.*, 1904, 203, 385; *Ibid.*, 1906, 205, 237.

DIFFRACTION OF COHERENT LIGHT BY DIFFUSING SURFACES

P. HARIHARAN

Indian Institute of Science, Bangalore-12

ABSTRACT

The rather unusual phenomena observed when diffusing surfaces are illuminated by coherent light have attracted considerable attention in the past few years. Recent work on the theory of these effects is briefly reviewed, and their principal features are examined. It is pointed out that similar effects were studied, and some of these conclusions were anticipated in earlier work by Professor Raman and his school.

CONSIDERABLE attention has centred in the past few years around the rather unusual phenomena observed when the beam from a continuous gas laser (such as a helium-neon laser) is scattered by a diffusing surface. The bright illuminated area then exhibits a remarkable granular appearance, not seen by ordinary light, and appears to scintillate or sparkle when there is relative motion of the surface and the observer^{1,2}. The scale of the granularity increases when the viewing distance is increased, and also when the relative aperture of the viewing system (the pupil of the eye, or the iris diaphragm of a camera) is decreased. On the other hand, the general appearance of the granularity is essentially independent of the character of the surface and the viewing distance. A photographic film exposed directly to the radiation scattered by the surface

records a random speckle pattern, as shown in Fig. 1.

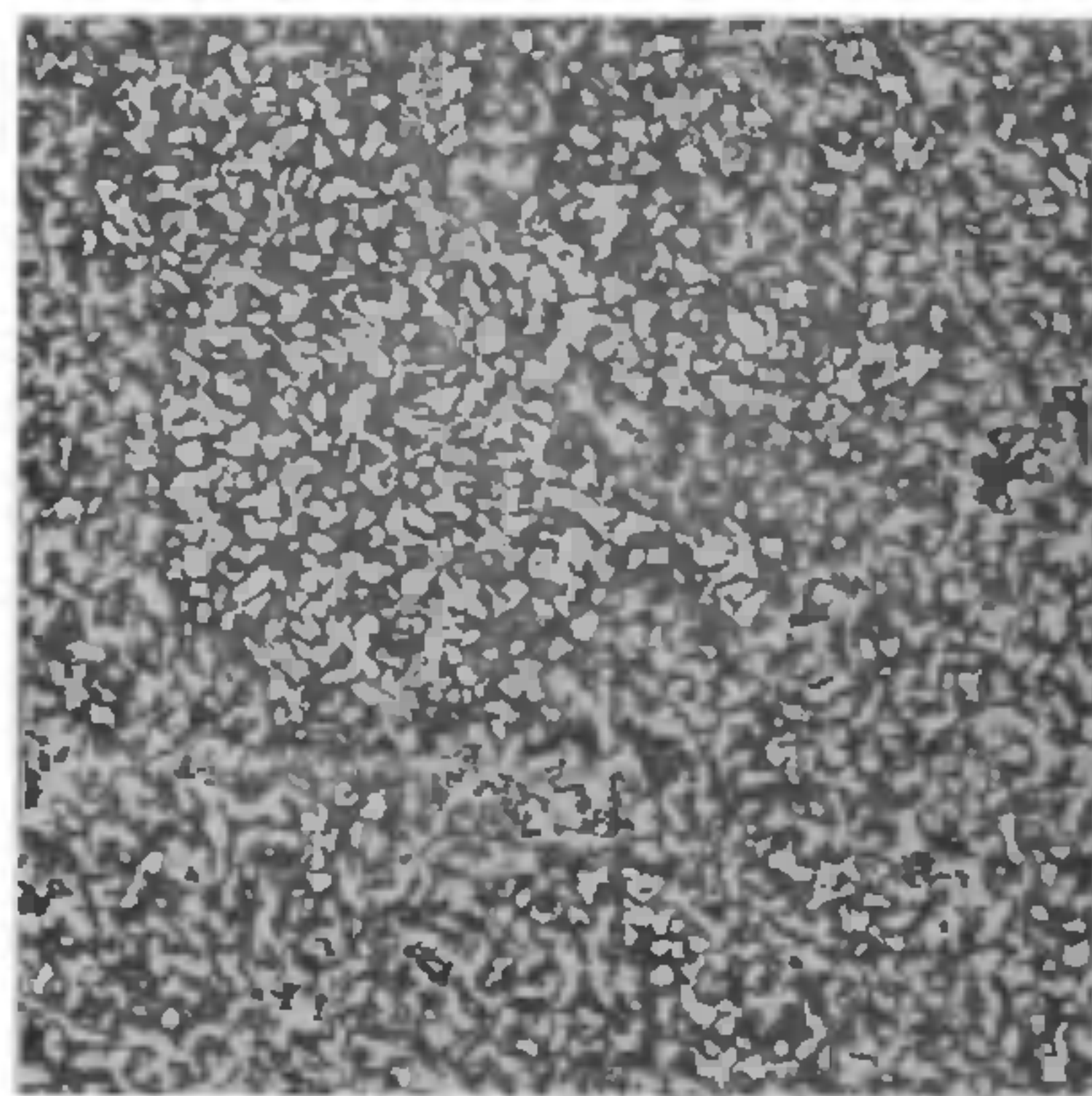


FIG. 1. Typical speckle pattern formed when a ground glass surface is illuminated by a coherent beam from a helium-neon laser.

The formation of such speckle patterns has been attributed to the high spatial