

Kirchhoff's Law of Thermal Radiation Has Not Been Violated

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Although violation of Kirchhoff's Law of Thermal Radiation has been claimed in a magneto-optic structure, it is shown that Kirchhoff's Law of Thermal Radiation has not been violated, noting that violation of Kirchhoff's Law of Thermal Radiation would imply that the Second Law of Thermodynamics has also been violated.

1. Introduction

Kirchhoff's Law of Thermal Radiation — often abbreviated as Kirchhoff's Law — has been exhaustively tested, without actual violation, since its formulation by Gustav Kirchhoff in 1860 [1]. Kirchhoff's Law of Thermal Radiation simply states that the absorptivity a of a body equals its emissivity e in thermal equilibrium. Thus, $a = e$ as shown in the classic text *Thermal Physics* by Kittel and Kroemer [2]. Before continuing, notice that Kirchhoff's Law is not expressed in terms of magnetic field B . In a footnote in his 1860 paper, Kirchhoff pointed out that his law does not apply in the presence of a magnetic field [1].

Kirchhoff's Law of Thermal Radiation applies in thermal equilibrium. Thermal equilibrium will be discussed with more nuance near the end of Section 2. In thermal equilibrium, the rate of absorption must equal the rate of emission [2]. If Kirchhoff's Law of Thermal Radiation was violated, then a given structure, left unperturbed, would either spontaneously heat up or cool down, implying a violation of the Second Law of Thermodynamics.

2. Claimed Violation of Kirchhoff's Law

In July 2023, in experimental work, Shayegan, Biswas, Zhao, Fan, and Atwater (SBZFA) reported nonreciprocity in spectral directional absorptivity and emissivity for a patterned magneto-optic structure and claimed this represented a violation of Kirchhoff's Law of Thermal Radiation [3]. It is argued here that Kirchhoff's Law has not been violated.

SBZFA measured the absorptivity and emissivity in their magneto-optic structure, shown in Fig. 1a in [3], when it was: (1) subjected to an actively switchable applied magnetic field from +1 T to -1 T that substantially differed from Earth's ambient surface magnetic field of $\sim 25\text{--}65\text{ }\mu\text{T}$ and (2) driven out of thermal equilibrium with the $24\text{ }^\circ\text{C}$ ambient by actively heating the structure to $100\text{ }^\circ\text{C}$ [3]. Right away — based on application of a switchable magnetic field and based on active heating of the structure such that thermal equilibrium was not achieved — we see that Kirchhoff's Law of Thermal Radiation does not apply to begin with. Since Kirchhoff's Law does not apply in the experiments conducted by SBZFA, it was not violated.

SBZFA specifically reported “the direct measurements of an inequality between the spectral directional emissivity and absorptivity for a photonic design that supports a guided-mode resonance coupled to a magneto-optic material.” At the structure's resonance wavelength ($\lambda = 12.65\text{ }\mu\text{m}$), SBZFA noted that “the magnetic field has an opposite effect for absorptivity and emissivity.” This was shown, separately, in Fig. 2c and Fig. 2d in [3]. Absorptivity and emissivity curves were not plotted together in a single full-size graph along with error bars and an uncertainty analysis to quantify the statistical significance of the small inequality between the spectral directional absorptivity and emissivity. Spectral emissivity was measured by SBZFA with a home-built angle-resolved thermal emission spectroscopy set-up whereas absorptivity was measured with a J.A. Woollam infrared ellipsometer [3].

Note that the sample developed by SBZFA was heated with a small-form resistive heater to $100\text{ }^\circ\text{C}$ “to enhance the signal-to-noise ratio” [3]. The operating temperatures of the thermal emission spectroscopy set-up and the infrared ellipsometer were not reported. The ambient temperature, though, was $24\text{ }^\circ\text{C}$ [3]. The totality of thermal radiation interacting with their $7\text{ mm} \times 7\text{ mm}$ sample from the $24\text{ }^\circ\text{C}$ ambient (as well as from any personnel running the experiments, noting that human body temperature is $37\text{ }^\circ\text{C}$) would effectively be a large source of thermal noise when compared to the small signal of spectral directional radiation from the sample over a narrow wavelength range centered at $12.65\text{ }\mu\text{m}$ and angle of 70° as shown in Fig. 2c and Fig. 2d in [3].

Moreover, if a steady-state applied magnetic field is set (e.g., -1 T) such that emissivity exceeds absorptivity at $12.65\text{ }\mu\text{m}$ in the structure for a sufficiently large angle of incidence (e.g., 70°) and also if a filter is included such that only $12.65\text{ }\mu\text{m}$ infrared (IR) radiation with an angle of 70° is absorbed and emitted whereas all other wavelengths and angles are reflected, then $e(12.65\text{ }\mu\text{m}) > a(12.65\text{ }\mu\text{m})$ implies that the structure can emit more radiation than it can absorb in the first place. Alternatively, if $a(12.65\text{ }\mu\text{m}) > e(12.65\text{ }\mu\text{m})$, then the structure would absorb more radiation than it emits, meaning that the ambient would be spontaneously cooled. This would represent a violation of the Second Law of Thermodynamics. It is also important to point out that the structure developed by SBZFA may be placed inside a cavity. To reach thermal equilibrium, the rate of absorption must equal the rate of emission and thus Kirchhoff's Law of Thermal Radiation is upheld.

If the structure is subjected to a transient nonequilibrium state due to a switchable applied magnetic field, a fluctuating radiation source, and/or a variable temperature, then Kirchhoff’s Law of Thermal Radiation would not be violated to begin with even if there is an inequality between absorptivity and emissivity since the law is valid under steady-state equilibrium conditions; i.e., the rate of absorption must balance the rate of emission in equilibrium [2,4]. The key term here is steady-state. A local form of Kirchhoff’s Law [5] may be applied to a body in quasi-equilibrium such as a steadily illuminated photovoltaic cell at the open circuit condition.

Regarding the relevant literature, we note that there have also been theoretical claims that Kirchhoff’s Law of Thermal Radiation can be violated. Although SBZFA investigated a patterned photonic structure containing a magneto-optic material [3], Pajovic, Tsurimaki, Qian, and Chen (PTQC) [6] as well as Wang, Javier García de Abajo, and Papadakis (WJP) [7] claim, in theoretical studies, that planar structures containing a magnetic Weyl semimetal layer can violate Kirchhoff’s Law. These Weyl semimetals have “magnetic-like effects” [7]. As mentioned in the Introduction, Kirchhoff’s Law of Thermal Radiation does not apply in the presence of magnetic fields [1]. Notably, counter to claims of violation of Kirchhoff’s Law, Han found, in a theoretical analysis, that thermal emission from photonic crystals does not violate Kirchhoff’s Law [8]. And, in a theoretical analysis of left/right reflectance asymmetry in a gyrotropic dielectric slab, there was no mention of violation of Kirchhoff’s Law [9].

3. Summary

Unperturbed structures are able to reach thermal equilibrium by absorbing and emitting thermal radiation in equal rates, and Kirchhoff’s Law of Thermal Radiation is simply a description of this outcome. The rate of absorption of thermal radiation must equal the rate of emission of thermal radiation in thermal equilibrium. In order to prove — at the most fundamental level — that Kirchhoff’s Law of Thermal Radiation has been violated, it must be demonstrated that a given structure does not reach thermal equilibrium when left unperturbed.

Shayegan, Biswas, Zhao, Fan, and Atwater (SBZFA) did not conclusively demonstrate a violation of Kirchhoff’s Law of Thermal Radiation with their magneto-optic structure. Rather than attempting to violate Kirchhoff’s Law, there are ways to engineer the emissivity of a given structure through surface modification while maintaining full compliance with Kirchhoff’s Law. This can take the form of texturing via mechanical abrasion or chemical etching, polishing to create high reflectance, application of evaporated or sputtered coatings, use of specialized paint, etc.

References

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