

A Generalized Expression for the Energy Density of Electromagnetic Waves in Media with Strong Temporal Dispersion

DAN ANDERSON

Research Laboratory of Electronics, Chalmers University of Technology, Gothenburg, Sweden

(Z. Naturforsch. 27 a, 1094-1098 [1972]; received 28 April 1972)

An expression is derived for the energy density of an electromagnetic wave of rather general form in a lossless, homogeneous and isotropic medium exhibiting temporal dispersion. The result is a generalization of the standard form and takes into account higher order derivatives of the dielectric and permeability functions as well as of the electric and magnetic field amplitudes of the wave. The classical derivation of the expression for the energy density given by BRILLOUIN¹, is discussed in some detail and, finally, a qualitative example of a chirp pulse in a simple medium is given, which illustrates the importance of higher order terms.

Introduction

The aim of the present article is to derive a generalized expression for the energy density of an electromagnetic wave in a temporally dispersive medium and to include terms of "higher dispersive order" i. e. terms containing higher derivatives of the envelope function of the waveamplitude and of dispersive functions like e. g. the dielectric function $\epsilon(\omega)$. This is in contrast to the normal treatment of problems connected with wavepropagation in dispersive media, which is of first dispersive order in the sense defined above.

The resulting, generalized expression for the energy density is quadratic in the wave-amplitude and its derivatives. It includes the standard result as the first term, to which it reduces, when the wave is taken to be monochromatic. A third order expansion is given, which should be sufficient for most practical purposes.

The analysis also demonstrates the very convenient use that can be made of the concepts of bilinear concomitants and adjoint operators from the theory of linear differential operators.

A detailed comparison is made with an example studied by BRILLOUIN¹. The present approach is shown to agree with his result. Some consequences of a higher order analysis are pointed out. The correction terms of the generalized expression for the energy density should be important for strong dispersion and/or broad band signals. This is qualitatively demonstrated with an example of a gaussian chirp pulse in a simple medium.

Reprint requests to D. ANDERSON, Research Laboratory of Electronics, Chalmers University of Technology, Göteborg, Sweden.

General Derivation

Starting from Maxwells equations for the electromagnetic field one identifies the energy density W as

$$\frac{\partial W}{\partial t} = E \frac{\partial D}{\partial t} + H \frac{\partial B}{\partial t}. \quad (1)$$

We shall study especially the electric part W_E of this expression, i. e.

$$\partial W_E / \partial t = E (\partial D / \partial t). \quad (2)$$

The magnetic part can of course be given a corresponding treatment. The dispersion is assumed to be temporal and we will consequently restrict the analysis to time-variations only. In that case the Fourier transforms of E and D are related as

$$D(\omega) = \epsilon(\omega) E(\omega) \quad (3)$$

where

$$X(\omega) = \int_{-\infty}^{+\infty} X(t) e^{-i\omega t} dt, \quad (4)$$

$$X = D, E \quad (5)$$

and $\epsilon(\omega)$ is the dielectric function. This implies that

$$\begin{aligned} \partial D / \partial t &= \int_{-\infty}^{+\infty} -i\omega \epsilon(\omega) E(\omega) e^{-i\omega t} d\omega \\ &= 2 \operatorname{Re} \int_0^{\infty} -i\omega \epsilon(\omega) E(\omega) e^{-i\omega t} d\omega \end{aligned} \quad (6)$$

where we have used the well known relations

$$\epsilon(-\omega) = \epsilon^*(\omega) \quad \text{and} \quad E(-\omega) = E^*(\omega).$$

Suppose now that we can expand $-i\omega \epsilon(\omega)$ in a Taylor series around the point ω_0 . For the moment this point can be considered arbitrary. Thus we have

$$-i\omega \epsilon(\omega) = \sum_{n=0}^{\infty} \frac{-i\omega \epsilon(\omega)}{n!} \left[\frac{\partial}{\partial \omega} (\omega - \omega_0) \right]^n \quad (7)$$

der überwiegende 3d-Metallcharakter dieser Orbitale wurde auch für Vanadocen, Ferrocen und Nickelocen gefunden⁶. Manganocen unterscheidet sich jedoch deutlich von diesen Verbindungen durch den Wert des Kovalenzfaktors: $k=0,9$. Durch Vergleich mit den von PRINS et al.⁷ angegebenen Werten $k=0,7$

für Vanadocen, $k=0,5$ für Ferrocen und $k=0,6$ für Nickelocen kann man schließen, daß Manganocen weniger kovalent gebunden ist. Dafür sprechen auch chemische Befunde und physikalische Messungen (Ultraspektrum, Massenspektrometrie, Suszeptibilitäts- sowie Leitfähigkeitsmessungen)⁴¹.

- ¹ R. E. ROBERTSON u. H. M. McCONNELL, J. Phys. Chem. **64**, 70 [1960].
- ² E. M. SHUSTOROVICH u. M. E. DYATKINA, Dokl. Akad. Nauk SSSR **128**, 1234 [1959]; **131**, 113 [1960]; **133**, 141 [1960]; J. Struct. Chem. SSSR **1**, 98 [1960]; **2**, 40 [1961]; **3**, 328 [1962].
- ³ J. P. DAHL u. C. J. BALLHAUSEN, Kgl. Danske Videnskab. Selskab. Mat. Fys. Medd. **33**, No. 5 [1961].
- ⁴ R. D. FISCHER, Theor. Chim. Acta **1**, 418 [1963].
- ⁵ A. T. ARMSTRONG, D. G. CARROLL u. S. P. MCGLYNN, J. Chem. Phys. **47**, 1104 [1967].
- ⁶ J. H. SCHACHTSCHNEIDER, R. PRINS u. P. ROS, Inorg. Chim. Acta **1**, 462 [1967].
- ⁷ R. PRINS u. J. D. W. VAN VOORST, J. Chem. Phys. **49**, 4665 [1968].
- ⁸ R. PRINS, J. Chem. Phys. **50**, 4808 [1969].
- ⁹ J. VOITLÄNDER u. E. SCHIMITSCHEK, Z. Elektrochem. **61**, 941 [1957].
- ¹⁰ M. NUSSBAUM u. J. VOITLÄNDER, Z. Naturforsch. **20 a**, 1411 [1965]; **20 a**, 1417 [1965].
- ¹¹ E. LUTZE, Z. Phys. Chemie **8**, 32 [1956].
- ¹² R. HOFFMANN, J. Chem. Phys. **39**, 1397 [1963].
- ¹³ M. WOLFSBERG u. L. HELMHOLZ, J. Chem. Phys. **20**, 837 [1952].
- ¹⁴ J. W. RICHARDSON, W. C. NIEUWPOORT, R. R. POWEL u. W. F. EDGELL, J. Chem. Phys. **36**, 1057 [1962]. — J. W. RICHARDSON, R. R. POWEL u. W. C. NIEUWPOORT, J. Chem. Phys. **38**, 796 [1963].
- ¹⁵ E. CLEMENTI u. D. L. RAIMONDI, J. Chem. Phys. **38**, 2686 [1963].
- ¹⁶ H. BASCH, A. VISTE u. H. B. GRAY, J. Chem. Phys. **44**, 10 [1966].
- ¹⁷ J. HINZE u. H. W. JAFFÉ, J. Amer. Chem. Soc. **84**, 540 [1962].
- ¹⁸ A. ALMENNINGEN, A. HAALAND u. T. MOTZFELDT, Selected Topics in Structure Chemistry, Universitetsforlaget, Oslo 1967, S. 105.
- ¹⁹ E. WEISS u. E. O. FISCHER, Z. Anorg. u. Allg. Chem. **284**, 69 [1956].
- ²⁰ P. O. LÖWDIN, J. Chem. Phys. **19**, 1570 [1951].
- ²¹ E. O. FISCHER u. H. LEIPFINGER, Z. Naturforsch. **10 b**, 353 [1955].
- ²² J. S. GRIFFITH, Mol. Phys. **3**, 79 [1960].
- ²³ J. H. VAN VLECK, Rev. Mod. Phys. **23**, 213 [1951].
- ²⁴ G. F. KOSTER u. H. STATZ, Phys. Rev. **113**, 445 [1959].
- ²⁵ F. A. COTTON, Chemical Applications of Group Theory, John Wiley, New York 1963.
- ²⁶ C. K. JÖRGENSEN, Orbitals in Atoms and Molecules, Academic Press, London 1962.
- ²⁷ B. N. FIGGS, Introduction to Ligand Fields, John Wiley, New York 1966.
- ²⁸ L. P. DAVE, Thesis, Imperial College, London 1959.
- ²⁹ D. A. LEVY, Thesis, Cambridge 1960.
- ³⁰ J. BJERRUM, C. J. BALLHAUSEN u. C. K. JÖRGENSEN, Acta Chem. Scand. **8**, 1275 [1954].
- ³¹ J. W. STOUT, J. Chem. Phys. **31**, 709 [1959].
- ³² H. L. SCHLÄFER u. G. GLIEMANN, Einführung in die Ligandenfeldtheorie, Akad. Verlagsges. Frankfurt (Main) 1967.
- ³³ R. M. PITZER, C. W. KERN u. W. N. LIPSCOMB, J. Chem. Phys. **37**, 267 [1962].
- ³⁴ R. MCWEENEY, J. Chem. Phys. **34**, 1065 [1961].
- ³⁵ R. E. WATSON, Phys. Rev. **118**, 1036, 1934 [1960].
- ³⁶ M. BLUME u. R. E. WATSON, Proc. Roy. Soc. London A **271**, 565 [1963].
- ³⁷ J. S. GRIFFITH, The Theory of Transition-Metal Ions, Cambridge University Press, London 1961.
- ³⁸ A. ABRAGAM, J. HOROWITZ u. M. H. L. PRYCE, Proc. Roy. Soc. London A **230**, 169 [1955].
- ³⁹ A. VAN HEUVELEN, M. D. LUNDEEN, H. G. HAMILTON u. M. D. ALEXANDER, J. Chem. Phys. **50**, 489 [1969].
- ⁴⁰ J. H. VAN VLECK, Phys. Rev. **74**, 1168 [1948].
- ⁴¹ G. WILKINSON, Inorg. and Nuclear. Chem. **2**, 95 [1956].
- ⁴² G. E. PAKE, Paramagnetic Resonance, W. A. Benjamin Inc., New York 1962.
- ⁴³ B. R. MCGARVEY, J. Phys. Chem. **61**, 1232 [1957].
- ⁴⁴ F. ENGELMANN, Z. Naturforsch. **8 b**, 775 [1953].
- ⁴⁵ M. F. RETTIG u. R. S. DRAGO, J. Amer. Chem. Soc. **91**, 1361, 3432 [1969].
- ⁴⁶ R. PRINS, Mol. Phys. **19**, 603 [1970].
- ⁴⁷ K. H. HELLWEGE, Einführung in die Festkörperphysik II, Springer-Verlag, Berlin 1970.
- ⁴⁸ A. ABRAGAM u. B. BLEANY, Electron Paramagnetic Resonance of Transition Ions, Clarendon Press, Oxford 1970.
- ⁴⁹ J. H. VAN VLECK u. W. G. PENNEY, Phil. Mag. **17**, 961 [1934].
- ⁵⁰ M. H. L. PRYCE, Suppl. Nuovo Cim. **6**, 817 [1957].

where $\bar{\partial}/\partial\omega$ denotes differentiation with respect to ω , working on $\omega \varepsilon(\omega)$ and evaluated at the point ω_0 . Artificially inserting in Eq. (6) the factor

$$1 = e^{-i\omega_0 t} e^{+i\omega_0 t} \quad (8)$$

it is possible to interpret powers of $\omega - \omega_0$ as time derivatives and we get

$$\frac{\partial D}{\partial t} = 2 \operatorname{Re} \left[e^{-i\omega_0 t} P \left(\frac{\partial}{\partial t} \right) \int_0^\infty E(\omega) e^{-i(\omega - \omega_0)t} d\omega \right] \quad (9)$$

where

$$P \left(\frac{\partial}{\partial t} \right) = \sum_{n=0}^{\infty} \frac{-i \omega \varepsilon(\omega)}{(-i)^n n!} \left[\frac{\bar{\partial}}{\partial \omega} \frac{\bar{\partial}}{\partial t} \right]^n. \quad (10)$$

Suppose the electric field to be given as

$$E(t) = \operatorname{Re} \{ E_0(t) e^{-i\omega_0 t} \}, \quad (11)$$

where ω_0 is the dominant frequency of the wave and $E_0(t)$ is a slowly varying amplitude. This may be expressed quantitatively as

$$\left| \frac{\partial}{\partial t} \ln |E_0(t)| \right| \ll \omega_0. \quad (12)$$

Comparing Eq. (11) with $E(t)$ in the general form

$$E(t) = \int_{-\infty}^{+\infty} E(\omega) e^{-i\omega t} d\omega = 2 \operatorname{Re} \int_0^\infty E(\omega) e^{-i\omega t} d\omega \quad (13)$$

we identify the envelope function $E_0(t)$ as

$$E_0(t) = 2 \int_0^\infty E(\omega) e^{-i(\omega - \omega_0)t} d\omega. \quad (14)$$

Inserting this in Eq. (9) gives

$$\frac{\partial D}{\partial t} = \operatorname{Re} \left\{ e^{-i\omega_0 t} P \left(\frac{\partial}{\partial t} \right) E_0(t) \right\}. \quad (15)$$

It is convenient to work with time averaged complex notations from here on. For that purpose we make a symmetrization of Eq. (2), i. e.

$$\frac{\partial W_E}{\partial t} = \frac{1}{4} \left(\tilde{E}^* \frac{\partial \tilde{D}}{\partial t} + \tilde{E} \frac{\partial \tilde{D}^*}{\partial t} \right) = \frac{1}{2} \operatorname{Re} \left\{ \tilde{E}^* \frac{\partial \tilde{D}}{\partial t} \right\} \quad (16)$$

where

$$X = \operatorname{Re} \tilde{X}; \quad X = E, \quad \partial D / \partial t.$$

This expression implies an averaging over time intervals long compared with the period of the fast variation, but short with respect to the variation of crossterms like $\tilde{E}^* (\partial \tilde{D} / \partial t)$. That this is a legitimate procedure is ensured by the condition expressed in Eq. (12).

Using Eq. (15), Eq. (16) can be rewritten as

$$\frac{\partial W_E}{\partial t} = \frac{1}{2} \operatorname{Re} \left\{ E_0^* P \left(\frac{\partial}{\partial t} \right) E_0 \right\} \quad (17)$$

with $P(\partial/\partial t)$ given by Equation (10).

Equation (17) for the electric part of the energy density is a quadratic expression in the amplitude and its derivatives. This implies that it will give a detailed treatment of the problem of dispersion due to higher order derivatives of the dielectric function as well as the amplitude of the wave.

It is obvious that a similar treatment can be given the magnetic part of the energy density W_H with the result

$$\frac{\partial W_H}{\partial t} = \frac{1}{2} \operatorname{Re} \left\{ H_0^* Q \left(\frac{\partial}{\partial t} \right) H_0 \right\} \quad (18)$$

where $H(t) = \operatorname{Re} \{ H_0(t) e^{-i\omega_0 t} \}$ denotes the magnetic field and $Q(\partial/\partial t)$ is obtained from Eq. (10) by replacing $\varepsilon(\omega)$ with $\mu(\omega)$, which is the permeability function. Finally we get

$$\frac{\partial W}{\partial t} = \frac{1}{2} \operatorname{Re} \left\{ E_0^* P \left(\frac{\partial}{\partial t} \right) E_0 + H_0^* Q \left(\frac{\partial}{\partial t} \right) H_0 \right\}. \quad (19)$$

Identification of the Energy Density

Equation (17) can be cast into a still more interesting form that is symmetrical and makes possible the identification of the energy density W_E itself.

The operator $P(\partial/\partial t)$ given by Eq. (10) is a linear differential operator with constant coefficients. It is easily verified that the following relation is valid

$$\bar{P} = -P^* \quad (20)$$

where \bar{P} is the operator algebraically adjoint to P . Furthermore we have the Lagrange identity (e. g. INCE²)

$$v P u - u \bar{P} v = \frac{\partial}{\partial t} C_P(u, v) \quad (21)$$

where $C_P(u, v)$ is the bilinear concomitant corresponding to P , and u and v are arbitrary functions. Putting $u = E_0$ and $v = E_0^*$ we obtain by means of Equation (20)

$$E_0^* P E_0 + E_0 P^* E_0^* = \frac{\partial}{\partial t} C_P(E_0, E_0^*). \quad (22)$$

Combining this with Eq. (17) we have

$$W_E = \frac{1}{4} C_P(E_0, E_0^*). \quad (23)$$

A similar treatment for the magnetic part finally gives the total energy density

$$W = \frac{1}{4} \{ C_P(E_0, E_0^*) + C_Q(H_0, H_0^*) \} \quad (24)$$

where C_Q is the concomitant corresponding to the magnetic operator $Q(\partial/\partial t)$ defined in connection with Equation (18). If we write out explicitly Eq. (23) to third order we get

$$W_E = \frac{1}{4} \frac{\partial(\omega \varepsilon)}{\partial \omega} E_0^* E_0 - \frac{1}{4} \frac{\partial^2(\omega \varepsilon)}{\partial \omega^2} \text{Im} \left(E_0^* \frac{\partial E_0}{\partial t} \right) - \frac{1}{24} \frac{\partial^3(\omega \varepsilon)}{\partial \omega^3} \left\{ \frac{\partial^2}{\partial t^2} (E_0^* E_0) - 3 \frac{\partial E_0^*}{\partial t} \frac{\partial E_0}{\partial t} \right\}. \quad (25)$$

The first term in this expression is the standard form for the energy density in a weakly dispersive medium (e. g. LANDAU and LIFSHITZ³). In addition we have two correction terms, which will be important, when we have a rapid variation of $\varepsilon(\omega)$ with ω and/or $E_0(t)$ with t .

The approach based on bi-linear concomitants and adjoint operators is very convenient in general studies of energy densities and energy flows in dispersive media, where a detailed analysis gives quadratic expressions like Equation (19). This general situation will be treated in a forthcoming paper.

Some Applications and Comparisons

A classical derivation of the standard formula for the energy density is given by BRILLOUIN¹. He emphasizes the fact that "in order to define a value of the energy in an oscillating field, it is necessary to consider a process which, starting at rest [$E(t) = 0$ for a certain time] slowly builds up to an os-

cillating field of amplitude a ". Brillouin gives an example of this by regarding the wave as a beat-wave during the build up phase. The electric field can thus be written

$$E(t) = \begin{cases} 0 & t \leq 0 \\ -a \sin \delta t \sin \omega t & 0 \leq t \leq \pi/2 \delta, \delta \ll \omega \\ -a \sin \omega t & t \geq \pi/2 \delta \end{cases} \quad (26)$$

and the energy W_E of the monochromatic wave $-a \sin \omega t$ is according to Brillouin

$$W_E = \int_0^{\pi/2 \delta} \left\langle E \frac{\partial D}{\partial t} \right\rangle dt = \frac{a^2 \partial(\omega \varepsilon)}{4 \partial \omega} \quad (27)$$

where we have neglected a factor $1/4 \pi$ due to cgs-units and $\langle \rangle$ denotes averaging over the fast variation determined by $\sin \omega t$. As pointed out by Brillouin the value obtained in Eq. (27) does not depend on δ and furthermore is "independent of the particular manner in which the amplitude varies" (during the build up phase), "as long as it is sufficiently slow".

We think it is instructive to consider the building up of a monochromatic wave by means of a general envelope function and take into account correction terms as given by Equation (25). In our notations we have for the envelope function $E_0(t)$.

$$E_0(t) = \begin{cases} 0 & t \leq 0 \\ e(t) & 0 \leq t \leq T, \quad 1/T \ll \omega \\ a/i & t \geq T \end{cases} \quad (28)$$

where $e(t)$ is a slowly varying function satisfying $e(0) = 0$ and $e(T) = a/i$.

From Eq. (25) we now have

$$W_E = \int_{-\infty}^t \frac{\partial W_E}{\partial t} dt = \int_0^T \frac{\partial}{\partial t} \left\{ \frac{1}{4} \frac{\partial(\omega \varepsilon)}{\partial \omega} e e^* - \frac{1}{4} \frac{\partial^2(\omega \varepsilon)}{\partial \omega^2} \text{Im} \left(e^* \frac{\partial e}{\partial t} \right) - \frac{1}{24} \frac{\partial^3(\omega \varepsilon)}{\partial \omega^3} \left[\frac{\partial^2}{\partial t^2} (e e^*) - 3 \frac{\partial e}{\partial t} \frac{\partial e^*}{\partial t} \right] \right\} dt. \quad (29)$$

To first order this gives

$$W_E = \frac{a^2 \partial(\omega \varepsilon)}{4 \partial \omega},$$

which of course coincides with Brillouin's result Eq. (27) and furthermore is in accordance with his general statement cited above. However, if we include higher order terms, it is obvious from Eq. (29) that the resulting value of the energy density will depend upon the values of the derivatives of $e(t)$ at the points $t=0$ and $t=T$. We are thus led to the

additional requirement that in a higher order analysis the chosen envelope function must be smooth enough, i. e. it should have continuous derivatives of sufficiently high order. E. g. for a third order analysis we must demand that

$$\frac{\partial e}{\partial t}(0) = \frac{\partial e}{\partial t}(T) = \frac{\partial^2 e}{\partial t^2}(T) = 0. \quad (30)$$

In that case the value of the energy density will still be given by Eq. (27) as it should.

For the purpose of a further comparison we want to compute the energy density of the wave given by Equation (26). In this case the envelope function is $e(t) = a \sin \delta t/i$ which inserted in Eq. (29) gives

$$W_E = \frac{a^2}{4} \left\{ \frac{\partial(\omega \varepsilon)}{\partial \omega} + \frac{\delta^2}{6} \frac{\partial^3(\omega \varepsilon)}{\partial \omega^3} \right\}. \quad (31)$$

It is interesting to note that this expression is obtained in an article by NICOLIS⁴, who extends Brillouin's analysis to third order and adds a statistical averaging based on the assumption that " δ is a statistically derived average value". Such an assumption is obviously not needed in the present analysis.

However it is easily seen that the envelope function $e(t) = a \sin \delta t/i$ is not smooth enough (in the sense defined above) for a third order analysis. Consequently the resulting value of the energy density Eq. (31) has no general significance.

A Qualitative Example

In this section we want to give an explicit example, which shows the importance of the correction terms. Consider for that purpose a general Gaussian pulse given by

$$E(t) = \frac{1}{2} E_0(t) e^{-i\omega_0 t} + \text{c.c.} \quad (32)$$

where

$$E_0(t) = A e^{-(\alpha - i\beta)t^2}; \quad 0 < \alpha. \quad (33)$$

The Gaussian envelope of the pulse is determined by the factor α and the term $i\beta t^2$ gives a linear frequency-shift during the pulse (chirp).

Pulses of this form have attracted considerable interest recently and have been studied e. g. in connection with the phenomena of mode locking of a laser (KUIZENGA and SIEGMAN⁵).

Assume a simple medium characterized by

$$\varepsilon(\omega) = 1 - \omega_p^2/(\omega^2 - \omega_c^2). \quad (34)$$

We want to show that under certain conditions the second term in Eq. (25) might very well be of the same order as the first, i. e.

$$\frac{\partial(\omega \varepsilon)}{\partial \omega} E_0 E_0^* \sim \frac{\partial^2(\omega \varepsilon)}{\partial \omega^2} \text{Im} \left(E_0^* \frac{\partial E_0}{\partial t} \right). \quad (35)$$

Make the further simplifying assumption that $|\omega_0 - \omega_c| \ll \min(\omega_c, \omega_p)$ and consider the special case of $\alpha = \beta$ corresponding to a FM-modulated signal (KUIZENGA and SIEGMAN⁵). Then relation

(35) implies

$$|\omega_0 - \omega_c| \sim \beta t. \quad (36)$$

But $1/t$ can be put equal to $\sqrt{\alpha}$, which is proportional to the band-width $\Delta\omega_0$ of the pulse and finally we have

$$|\omega_0 - \omega_c| \sim \Delta\omega_0. \quad (37)$$

From this result we draw the following conclusions; For a broad signal ($\Delta\omega_0$ great) the correction terms will contribute already far from resonance, but with a narrow signal ($\Delta\omega_0$ small) the carrier frequency ω_0 must lie near the resonance frequency ω_c for the correction term to become important.

Acknowledgements

I want to thank Professor O. E. H. RYDBECK for suggesting the subject and Dr. J. ASKNE for his kind interest and valuable advice during the preparation of the article.

Appendix

Inserting the Taylor-expansion, Eq. (7), into the integral Eq. (6), actually requires some care, because associated with the Taylor-expansion is a certain radius of convergence, R , which is given by

$$\frac{1}{R} = \lim_{n \rightarrow \infty} \left[\frac{1}{n!} \left| \frac{\partial^n(\omega \varepsilon)}{\partial \omega^n} \right| \right]^{1/n}. \quad (\text{A:1})$$

When R is finite, the expansion cannot be used directly in the integral, Eq. (6), which extends from 0 to infinity. The use of the Taylor series can however be justified if we require that $E(\omega)$ has compact support within the convergence domain, i. e. we have the set relation:

$$\{\omega; E(\omega) \neq 0\} \subset \{\omega; |\omega - \omega_0| < R\}. \quad (\text{A:2})$$

This is qualitatively in accordance with the requirement of a slowly varying envelope function expressed by Eq. (12).

The condition of compact support can be relaxed in order to meet the requirements of a more practical situation. The integral in Eq. (6) is finite, being equal to $\partial D/\partial t$. Suppose then that the contributing part of the integrand comes from a domain located around ω_0 , in the sense that for each $\delta > 0$ we can find an $N(\delta) > 0$ such that

$$\left| \int_J \omega \varepsilon(\omega) E(\omega) e^{-i\omega t} d\omega \right| < \delta \quad (\text{A:3})$$

where $J = \{\omega; |\omega - \omega_0| > N, \omega > 0\}$. If $N(\delta) < R$ for an acceptable degree of accuracy, as determined by δ , then the insertion of the Taylor expansion and the procedure leading to Eq. (9) is legitimate.

Finally we note that the relation, Eq. (A:2) becomes more restrictive when dispersion becomes strong.

- ¹ L. BRILLOUIN, Wavepropagation and Group Velocity, Academic Press, London 1960.
- ² E. L. INCE, Ordinary Differential Equations, Longmans, Green and Co., Dover 1944.
- ³ L. D. LANDAU and E. M. LIFSHITZ, Electrodynamics of Continuous Media, Pergamon Press, London 1960.
- ⁴ I. S. NICOLIS, The Velocity of Energy Transport for Normal Modes Near Total Internal Reflection, Z. Naturforsch. **26 a**, 124 [1971].
- ⁵ D. J. KUIZENGA and A. E. SIEGMAN, FM and AM Mode Locking of the Homogeneous Laser, Part I: Theory, IEEE J. Quantum Electronics, Vol. Q E-6, No. 11, p. 694 [1970].

Abschätzung von Zustandsdichten des Silbers in α -Silber-Mischkristallen mit Gallium, Indium, Germanium und Zinn auf Grund thermodynamischer Untersuchungen mittels galvanischer Festkörperzellen

B. PREDEL und U. SCHALLNER

Institut für Metallforschung der Universität Münster (Westf.)

(Z. Naturforsch. **27 a**, 1098—1108 [1972]; eingegangen am 23. März 1972)

An Estimation of Densities of State of Silver in α -Solid Solutions of Silver with Gallium, Indium, Germanium and Tin based on Thermodynamic Investigations by means of Solid State Galvanic Cells

The partial free enthalpies of formation of the binary α -solid solutions of silver with gallium, indium, germanium and tin were determined at 1000 °K from the EMF of suitable solid state galvanic cells. A further evaluation of the results taking into account known enthalpies of formation yielded the complete partial and integral excess functions of these solid solutions.

An analysis of the difference of the excess values of the partial free enthalpies of formation of the components showed that the lattice distortion, due to differences in atomic radii of the solid solutions studied, is not very significant. Differences in the structure between the solid solution and its components can be clearly noted only in the case of the silver-germanium solid solutions. The energetics of the alloys are determined principally by the filling of the $5s^1$ conduction band of the silver by the electrons contributed by higher-valent constituents. From the thermodynamic results the density of state of the conduction band of the silver was estimated to be smaller than 0.31 electr. per atom and eV. The density of state increases with increasing concentration of the alloying component; this can be explained by a change in the Fermi surface in the silver host lattice.

Einführung

In zahlreichen neueren Untersuchungen wird der Frage nachgegangen, welche Faktoren in einem individuellen metallischen Zweistoffsystem für die energetischen Verhältnisse der jeweiligen Mischphasen verantwortlich sind. Es hat sich dabei als zweckmäßig erwiesen, die Überschuffunktionen als in einfacher Weise additiv aus Einzelanteilen zusammengesetzt zu betrachten, die von den jeweiligen einzelnen Einflußgrößen herrühren. In der Regel werden dabei drei verschiedene Einflüsse betrachtet, die zweifellos nur modellmäßig scharf voneinander getrennt werden können¹⁻³. Von wesentlicher Bedeutung ist in vielen Fällen die Änderung der chemischen Bindungsverhältnisse bei der Legierungsbildung. Daneben kann im Falle großer Atomradiendifferenzen der Legierungspartner auch die Gitterverzerrung in festen Mischphasen von Bedeutung

sein. Schließlich können sich noch strukturelle Unterschiede auf die energetischen Eigenschaften einer Legierung auswirken, wenn die betrachtete Mischphase nicht isotyp ist mit den Gitterstrukturen der Partner.

Zur Abschätzung der Gitterverzerrungseinflüsse sind an Hand von Modellen Näherungsrechnungen entwickelt^{4,5} sowie empirische Methoden zur Erschließung von Fehlpassungseinflüssen aufgezeigt worden⁶. Der strukturelle Einfluß, der sogenannte Umwandlungsanteil, kann durch Auswertung experimentell ermittelter Mischungsenthalpien und Überschubentropien entsprechender Systeme ermittelt werden^{3,7}. Eine vollständige Klärung des „Bindungsanteils“ ist indessen bisher nur in wenigen Fällen in quantitativer Weise gelungen. Das ist bei der Vielzahl an individuellen Möglichkeiten der oft recht komplexen Bindungsverhältnisse in metallischen Systemen nicht verwunderlich.

Bei einer großen Anzahl von Legierungen kann bekanntlich eine Reihe physikalischer Eigenschaften an Hand des Bändermodells erklärt werden. Es er-