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QUANTITATIVE INTERPRETATION OF TG AND DTG CURVES OBTAINED FOR SOME FERROMAGNETIC SUBSTANCES IN LOW INTENSITY A.C. GENERATED MAGNETIC FIELD

R. MOSKALEWICZ
Polfer Research Laboratory, Dzielna 60, 01-029 Warsaw (Poland)
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ABSTRACT

Earlier studies on the possibility of magnetochemical analysis, employing a simultaneous TG–DTG–DTA method, have been extended. Several magnetic samples of different chemical compositions, e.g. spinels, garnets and hexagonal ferrites, were examined. Investigations involved both soft ($NiFe_2O_4$, Mn–Mg ferrite, $Y_3Fe_5O_{12}$) and hard magnetic materials such as $BaFe_{12}O_{19}$, $SrFe_{12}O_{19}$. The capability of the method, referred to in the following as DTMG, for the qualitative and the quantitative analysis of a wide variety of magnetic materials is proposed. The results are discussed in terms of the basic magnetic parameters such as a magnetocrystalline anisotropy, magnetic moment and ferromagnetic Curie point temperature, T_c. The relationship between DTMG line intensities and concentrations of the respective magnetic substances was found. The results are interpreted on the basis of the Curie point measurements by means of DTMG curves in the temperature range between 20 and 1200°C. It is a proposal to call the TG and DTG curves taken simultaneously in the presence of an alternating magnetic field as the TMG and DTMG curves, respectively. The term DTMG stands for Derivative Thermo - Magneto - Gravimetry. The idea of the method has been developed in this laboratory.

The DTMG method is capable of good precision within resonable time. The method can be applied to polycrystalline as well as to single crystals of the magnetic materials and the sample can be in the solid or powder state.

INTRODUCTION

The purpose of this work is to show the possibilities of the DTMG method for Curie point measurements and, at the same time, for the determination of intermediate and final magnetic phases content. Of the numerous parameters which require close control during and after ferrite preparation, chemical composition, grain size and its distribution, saturation magnetization, lattice constant and Curie point temperature are of major importance in controlling the factors which decide the quality of the sintered product. The magnetic properties of a given ferro- or ferrimagnetic substance may be divided into two classes. The first contains properties such as permeability and coercive force which are determined by technological processing variables or sample configuration. The second contains properties such as magnetic moment (or saturation magnetization per unit weight, σ e.m.u./g) and Curie point temperature, T_c. The last two parameters would remain unchanged even if the sample were powdered. If the ferromagnetic sample contains more than one magnetic phase, as it frequently does in ferrite and garnet solid solutions, it is hard to detect them by saturation magnetization versus temperature measurements. In many cases, it is impossible to determine the Curie point T_c from magnetization measurements because the curve exhibits a large "tail" near the transition temperature T_c. The reason is not certain but it is expected that the cation distribution, i.e. ordering or inhomogeneity, plays an important role. In such cases, the DTMG method indicates that some additional magnetic phases may be present in the sample. Very often these additional phases cannot be evaluated by magnetization measurements or by conventional chemical and X-ray diffraction analyses. It is well known that wet chemical analysis does not give an answer on the homogeneity of a given magnetic substance. Moreover, the X-ray powder diffraction pattern in some cases does not reveal all the magnetic phases present in the sample. This is because the differences in the lattice parameters among the magnetic phases are frequently very small, especially in the case of mixed ferrites and garnets in which one or more multivalent element is present.

EXPERIMENTAL

The experiments were performed on a Derivatograph MOM in a static atmosphere of air. The samples varied in weight from 100 to 1000 mg and the grain size from −80 mesh to −60 mesh. The temperature was programmed linearly at 8°C/min between 20°C and 1200°C. The samples were placed in a standard platinum crucible. The furnace served as a heating element and, at the same time, as an alternating magnetic field source. The intensity of the alternating magnetic field was measured by means of a coil and millivoltmeter. The amplitude of the magnetic field was evaluated for about 55 Oersteds and the frequency, f, was 50 Hz. The field intensity had its maximum in the central part of the furnace and decreased towards both ends, thus giving rise to a field gradient. The field gradient was present inside the furnace and a force acted on a properly situated ferromagnetic sample. In the case of the hard magnetic materials, all experiments were made on thermally demagnetized samples. During experiments, no chemical reactions (reduction or oxidation) were observed on TMG and DTMG curves nor on the DTA.

RESULTS AND DISCUSSION

Ferrospinels, garnets and hexagonal ferrites play an important rule in the field of the solid state electronics[1, 2]. The required properties are defined by chemical composition, crystal structure and by grain microstructure. The knowledge of the chemical composition and its deviation from stoichiometry is of technological and theoretical importance for all magnetic materials.

Preliminary investigations[3, 4] indicated that the DTMG method for magnetochemical studies offered excellent possibilities. The present paper discusses the possibility of determining the magnetic phase content from DTMG curves obtained in the presence of the alternating magnetic field. The idea of the DTMG method presented here can be summarized as follows. If a sample containing some quantity of a ferromagnetic or ferrimagnetic substance is being analysed thermogravimetrically in the presence of the alternating magnetic field, two distinct peaks appear on the DTMG curve. The first is an upward peak which corresponds to an apparent weight gain immediately after the alternating magnetic field is applied. This initial peak appears at ambient temperature for all magnetic substances, even if the magnetic moment per unit weight of a given sample is very low. The intensity of the initial peak seems to be dependent on the magnetocrystalline anisotropy and, in consequence, on the coercive force of the sample. The higher the coercive force, the lower the intensity of the initial DTMG peak. The above statement was confirmed by many experiments and found its confirmation on the DTMG curves taken for hard and soft magnetic materials. More work is needed to completely resolve the dependence of the initial DTMG peak intensity on the particular magnetic properties. The second DTMG peak, a downward one, corresponds to the ferro-to-paramagnetic transition at the Curie point temperature, T_c. The change from the ferromagnetic to the paramagnetic state is perfectly sharp, and is easy to define and determine the Curie point very precisely.

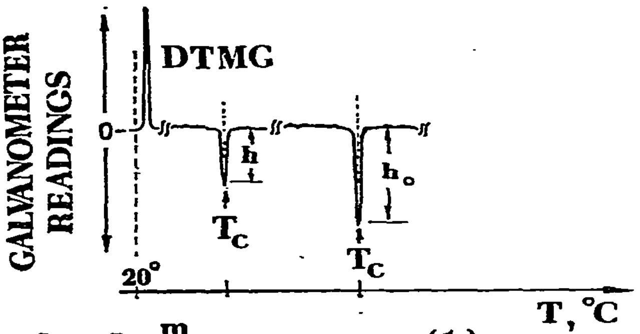
For magnetically hard substance, e.g. $BaFe_{12}O_{19}$ or $SrFe_{12}O_{19}$, the second, or shorter, "T_c peak" is preceded by another, again an upward peak, the origin of which seems to be related to the particularly sharp dependence of the magnetocrystalline anisotropy[5] near the Curie point, T_c. This will be discussed later.

It was found and confirmed by many experiments that the intensity of the T_c peak is directly dependent on the amount of the magnetic phase present in the sample. The dependence is shown schematically in Fig. 1 and can be expressed as

$$h = km/s \tag{1}$$

where h is the T_c peak intensity (mm), m the mass of the magnetic phase (mg), s the DTMG sensitivity (μV/mm) and k the proportionality coefficient (μV/mg). It is of crucial importance that the T_c peak intensity does not depend on the presence of the other phases either magnetic or nonmagnetic, unless corresponding T_c peaks overlap. In practice, cases of overlapping peaks of different magnetic substances are not frequent.

Another important feature of the method is the possibility of a very accurate determination of the Curie points, T_c, for a single magnetic phase as well as for a mixture of different magnetic phases. Since the Curie points for most ferro- and ferrimagnetics are known with sufficient accuracy, the T_c values, properly catalogued[6, 7], can be utilized for phase identification. This can also be done when the



$$h = k\cdot\frac{m}{s} \quad \text{-------} \quad (1)$$

h-T_c peak intensity [mm]
m–mass of the magnetic phase [mg]
s–DTMG sensitivity [μV/mm]
k–proportionality coefficient [μV/mg]

$$h_o = k\cdot\frac{m_o}{s_o} \quad \text{----------} \quad (2)$$

$$m = \frac{s\cdot h}{s_o h_o}\, m_o \quad \text{----------} \quad (3)$$

$$w = \frac{m}{m_s} = \frac{s\cdot h\cdot m_o}{s_o h_o m_s} \quad \text{-----} \quad (4)$$

$$w = \frac{A}{A_o} \quad \text{----------} \quad (5)$$

Fig. 1. Schematic representation of the relationship between T_c peak intensity and amount of a magnetic phase in a ferromagnetic sample.

relation between the chemical composition and the Curie point of a given magnetic substance, e.g. $Y_3Fe_{5-x}Ga_xO_{12}$ (GaYIG) is known. In such cases, it is possible to control the gallium substitution level. The magnetic phase having been identified, it is quite simple to obtain a standard DTMG plot for the pure substance to be determined. Equation (1) being valid, we can write for the standard sample

$$h_0 = km_0/s_0 \tag{2}$$

From eqns. (1) and (2), the coefficient k can be eliminated and then m expressed by

$$m = \frac{sh}{s_0 h_0} m_0 \tag{3}$$

If the total mass of the sample is m_s, the weight fraction of the magnetic phase is

$$w = \frac{m}{m_s} = \frac{shm_0}{s_0 h_0 m_s} \tag{4}$$

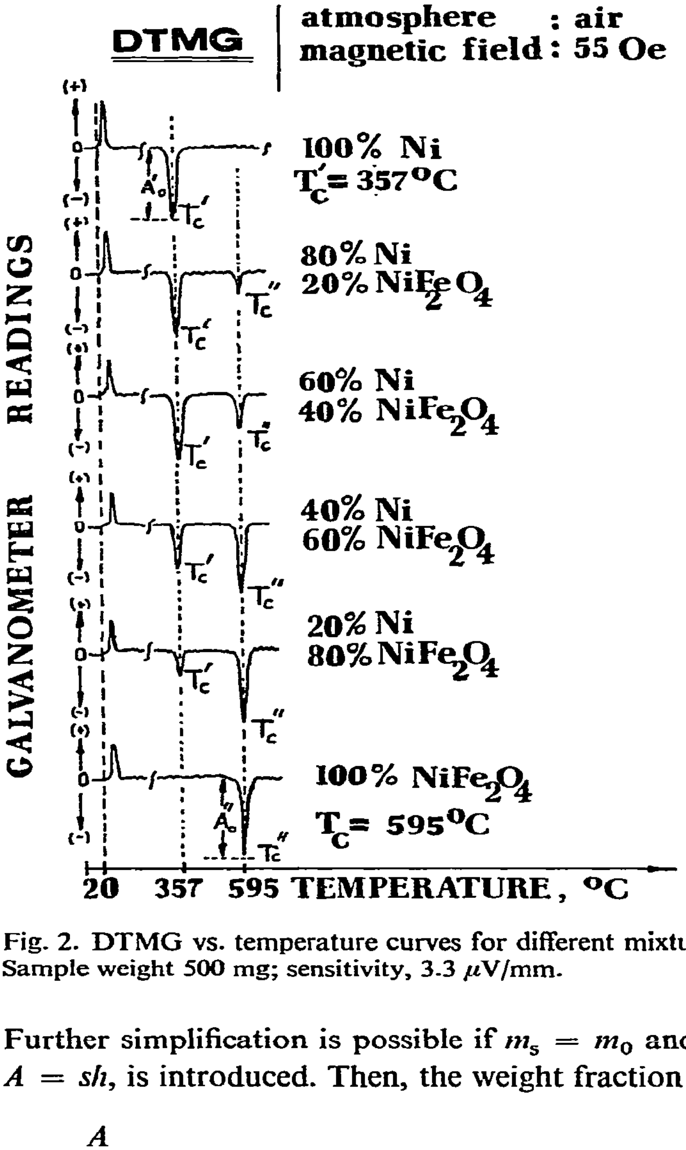


Fig. 2. DTMG vs. temperature curves for different mixtures of nickel and nickel ferrite, $NiFe_2O_4$. Sample weight 500 mg; sensitivity, 3.3 μV/mm.

Further simplification is possible if $m_s = m_0$ and the T_c peak amplitude, defined as $A = sh$, is introduced. Then, the weight fraction w is

$$w = \frac{A}{A_0} \tag{5}$$

It is obvious that, for the method to be applicable, no chemical reaction should take place up to the Curie point, T_c.

As an illustration of the procedure described, Fig. 2 shows a series of DTMG curves obtained for a number of mixtures of known composition containing two magnetic phases, namely pure metallic nickel, Ni (Johnson Matthey Chemicals Ltd.) and nickel ferrite, $NiFe_2O_4$, prepared in our laboratory by conventional ceramic technique (sintered at 1200°C in air for 5 h). Chemical and X-ray examinations showed no foreign phases.

The applicability of the method has been tested on both the polycrystalline form and single crystals of the magnetic materials. In Fig. 3, the juxtaposition of the two experimental curves, i.e. the DTMG (curve "a") and saturation magnetization vs.

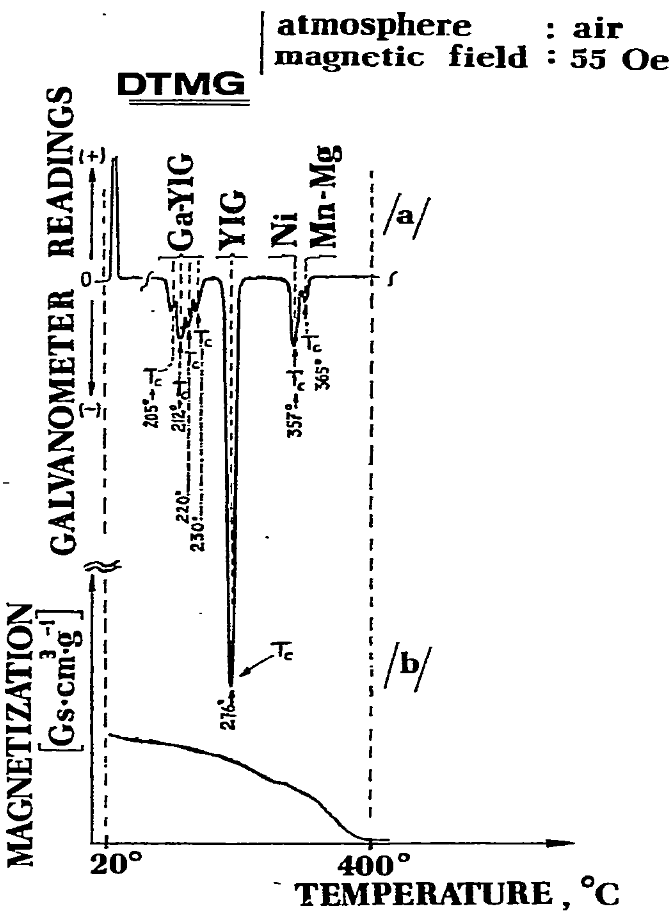


Fig. 3. DTMG (curve "a") and magnetization vs. temperature (curve "b") curves taken for the same mixture of GaYIG, YIG, Ni and Mn–Mg ferrite. Sample weight, 680 mg; sensitivity, 3.3 μV/mm.

temperature (curve "b") taken for the same mixture is shown. The mixture had the following composition (wt. %): single crystals of yttrium iron garnet with substitution of gallium, $Y_3Fe_{5-x}Ga_xO_{12}$ ($x = 0.5$) 16.2, yttrium iron garnet single crystal, $Y_3Fe_5O_{12}$, 74.3, metallic nickel, Ni, 6.9 and Mn–Mg ferrite 2.5. The powdered (— 80 mesh) components were mixed in the proportion shown. The single crystals were grown in this laboratory from lead oxide, lead fluoride and lead borate fluxes by slow cooling technique (flux method). The comparison of the two curves clearly justifies the statement that the accuracy in determining the Curie point T_c from DTMG plots is much higher than that based on the analysis of the magnetization versus temperature curves. Moreover, the four T_c peaks, as seen on DTMG curve Fig. 3a, indicate a different gallium distribution within the bulk (as grown) single crystal of GaYIG garnet. The above conclusion derived from the DTMG analysis was also confirmed by ferrimagnetic line width measurements, ΔH. With this technique, it is also possible to distinguish between two magnetic phases that differ in their Curie points by less than 8 °C. Such a case is also shown in Fig. 3a for the metallic nickel, Ni, and Mn–Mg ferrite. Unlike the soft magnetic materials (low magnetocrystalline aniso-

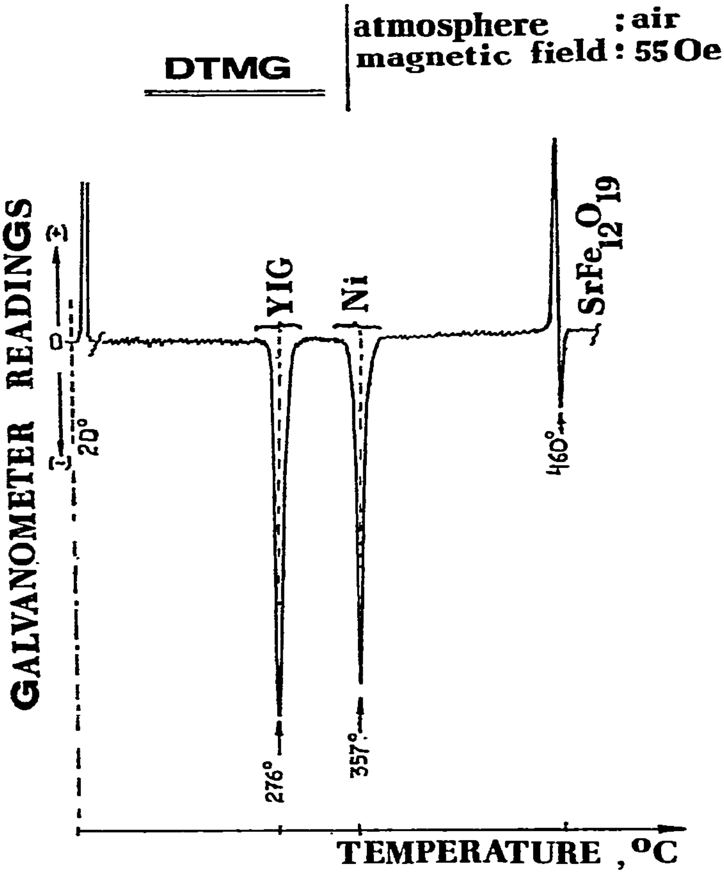


Fig. 4. DTMG vs. temperature curves for a mixture of soft and hard magnetic substances, YIG, Ni and $SrFe_{12}O_{19}$. Sample weight, 1200 mg: sensitivity, 2.2 μV/mm.

tropy), the hard ferromagnets like $SrFe_{12}O_{19}$ or $BaFe_{12}O_{19}$ exhibit an interesting phenomenon, i.e. an upward peak that appears in the neighbourhood of the Curie point as seen on the DTMG curve (Figs. 4 and 5). Besides the Curie point temperature, this is an additional factor that allows one to distinguish the two kinds of magnetic material when present in the same sample. A typical run of the DTMG curve for the powdered mixture of the hard and soft magnetic substances is shown in Fig. 4. From this curve it can be seen that the sample is composed of three magnetic phases. Moreover, two of them are soft magnetic materials and the other is a hard magnetic substance.

The above mentioned sample (see Fig. 4) was prepared by mechanical mixing of the following constituents: 25 wt.% yttrium iron garnet single crystal, 25 wt.% metallic nickel and 50 wt.% polycrystalline $SrFe_{12}O_{19}$. The strontium ferrite powder (− 80 mesh) was prepared by crushing the pellets in an agate mortar and its coercive force was $_IH_c = 3000$ Oe as measured on the sintered product.

Another interesting phenomenon for the hard magnetic materials in the vicinity of the Curie point temperature is shown in Fig. 5 (samples No. 1 and 2). The samples were powdered (− 60 mesh) and analysed under the same experimental

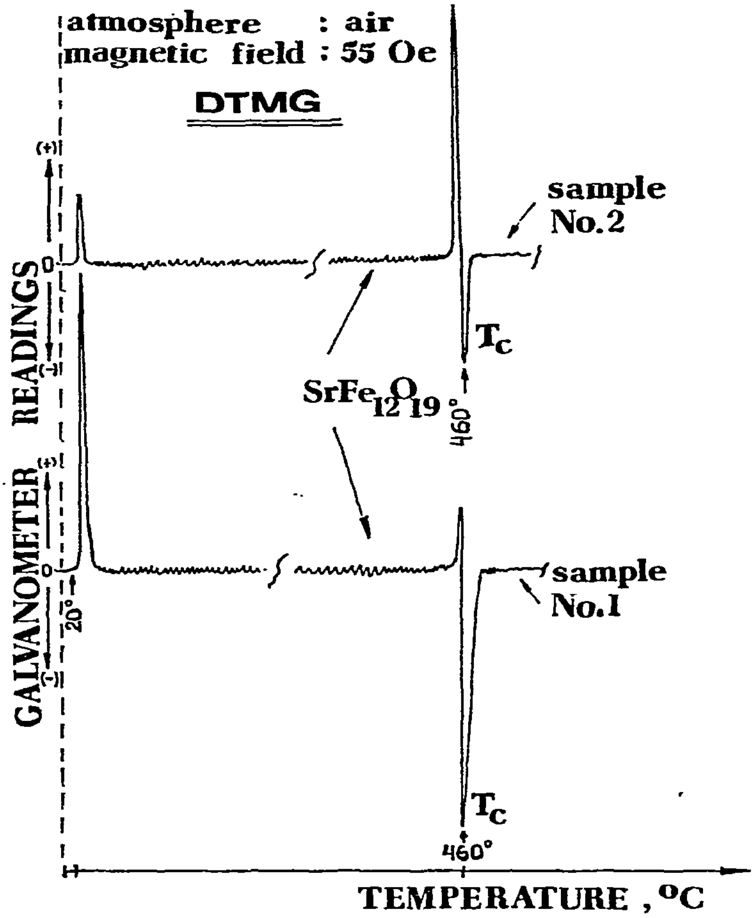


Fig. 5. DTMG vs. temperature curves for $SrFe_{12}O_{19}$ with different coercive force values. Sample weight, 600 mg: sensitivity, 2.2 μV/mm.

conditions. The coercive force of sample No. 1 was $_{j}H_{c}$ = 500 Oe and for sample No. 2, $_{j}H_{c}$ = 4000 Oe as measured on the pellets. The results reveal unexpected dependence of the peak intensity (an upward one) on the coercive force value. It is clearly seen on the DTMG curve that for the sample with a higher coercive force, the upward peak is also higher. In addition, from Fig. 5 it can be seen that the intensity of the initial DTMG peak also depends on the value of the coercive force of the sample. As the coercive force of the sample increased, the intensity of the initial DTMG peak decreased. No explanation of such behaviour can be given at present. It seems that full analysis of the curves can reveal physical information about the nature of the internal magnetic processes within the hard magnetic substances. Hence, the DTMG method is presented as one which is complementary to conventional DTA, wet chemical analysis, X-ray and some purely magnetic methods, i.e. magnetization or permeability versus temperature measurements. It is clear that the method has many limitations and needs some refinement. A theoretical analysis is also necessary. Further work on the subject is in progress.

CONCLUSIONS

The DTMG method, which is similar, in principle, to the well known TG–DTG–DTA complex analysis, has several important advantages. Results indicate that the DTMG method can become a valuable tool for qualitative and quantitative analysis of the magnetic substances in the positive temperature range. Since the T_c peaks are well pronounced on the DTMG curve (much better than on DTA or magnetization vs. temperature curves), it is easier to determine the Curie points. The method can be applied to polycrystalline material as well as to single crystals and the sample can be in the solid or in powdered state. The magnetic substances that differ in their Curie points by not less than 8 °C can be easily distinguished from each other without any difficulties. The relative simplicity of DTMG analysis makes the method exceedingly effective for the magnetochemical analysis of multicomponent mixtures or compounds such as are found in ferrites, garnets and the like. The method described is suitable for both soft and hard magnetic substances. In the case of hard magnetic materials, the DTMG curve exhibits an interesting phenomenon in the vicinity of the Curie point, i.e. an upward peak that appears on the DTMG curve just before the T_c peak temperature. Its origin cannot be explained qualitatively at present, but it seems likely that it is associated with the sharp temperature dependence of the magnetocrystalline anisotropy and saturation magnetization in the neighbourhood of the ferromagnetic transition region. The accuracy in determining the Curie point was estimated to be better than 2 °C with high reproducibility and resolution. The T_c peak intensity does not depend on the presence of the other phases unless corresponding peaks overlap.

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