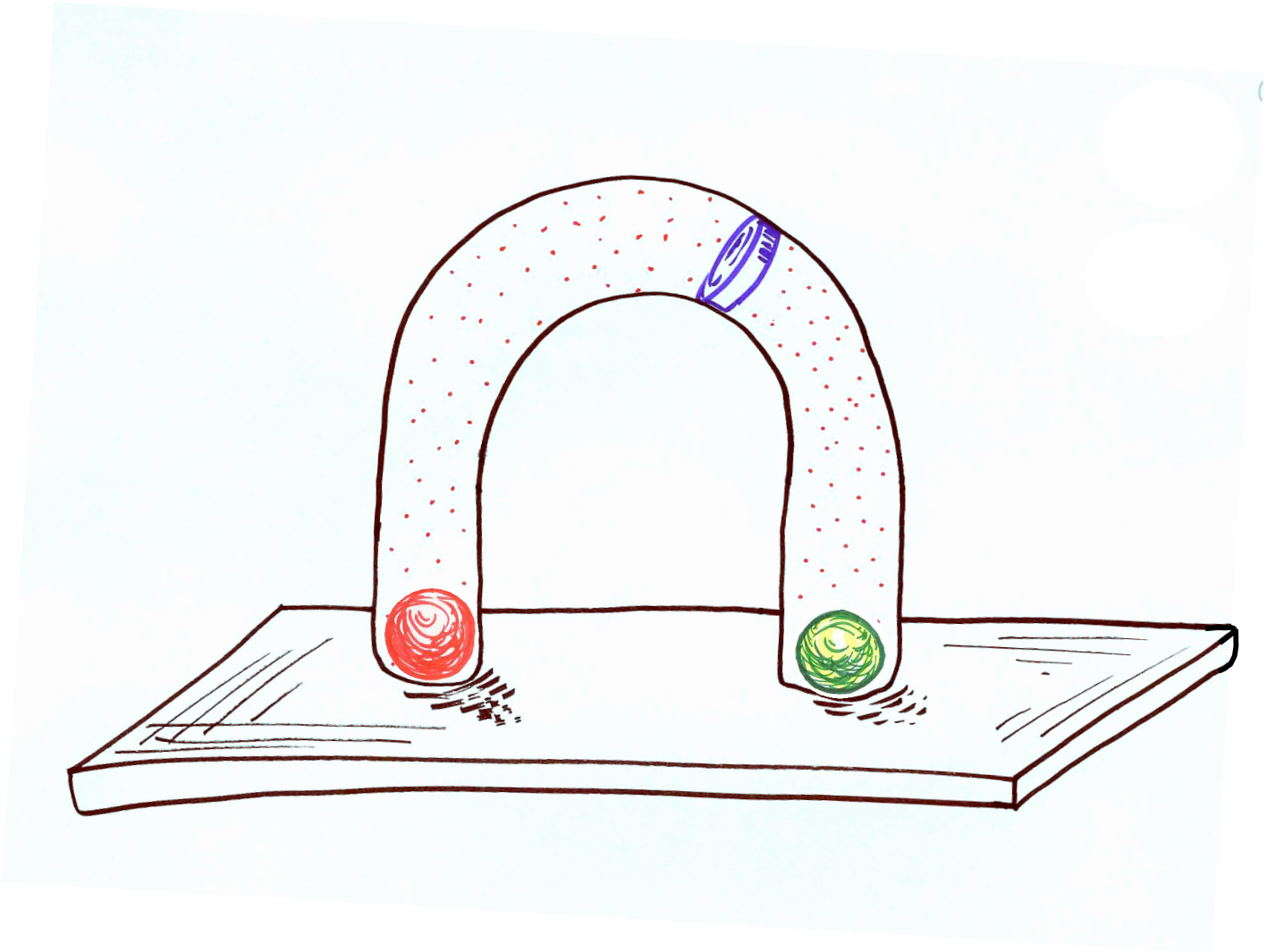
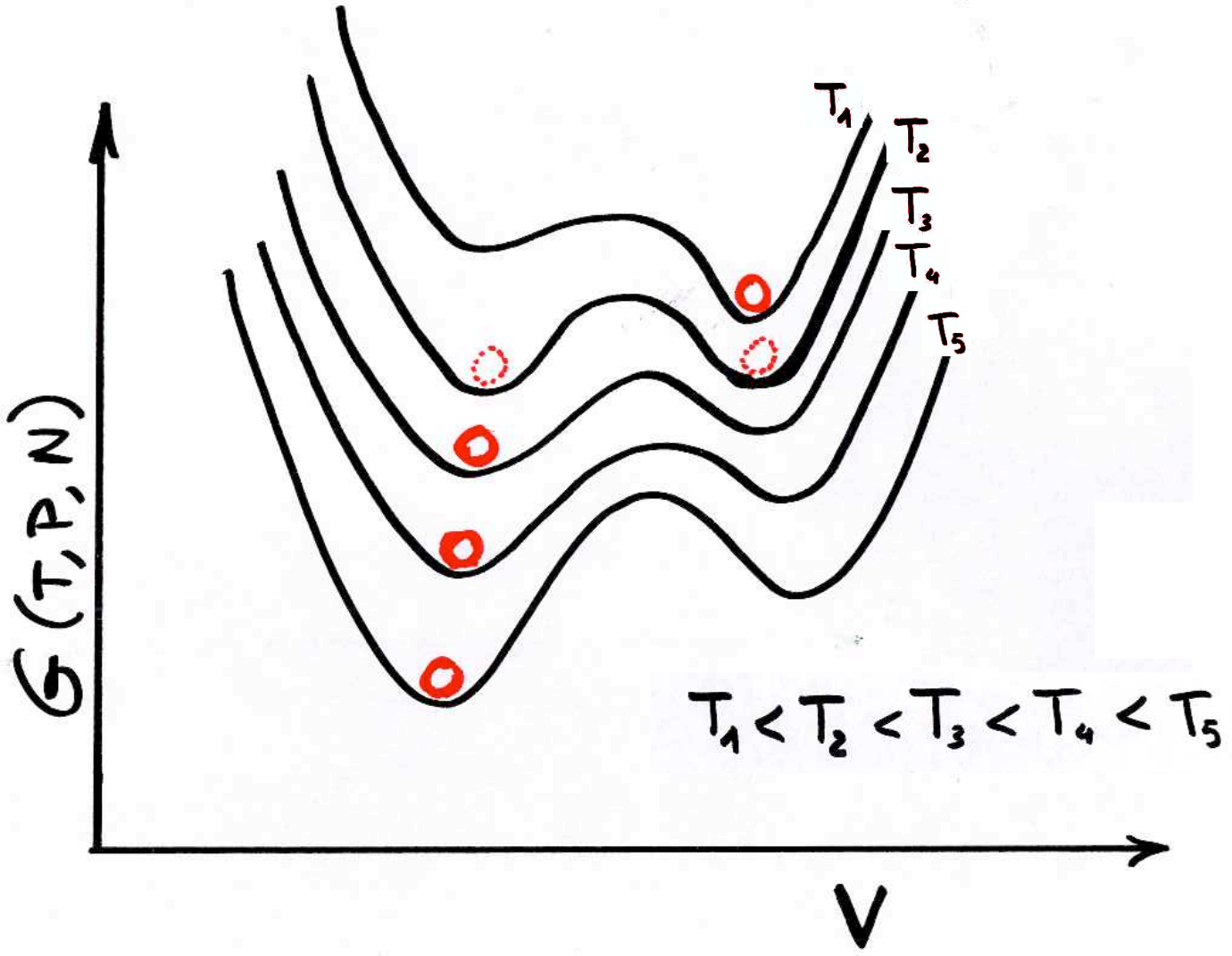
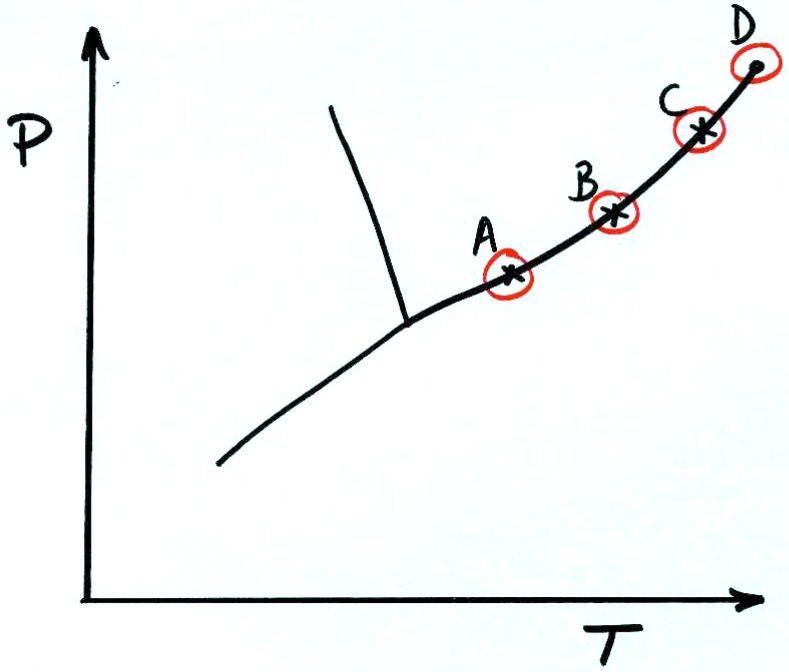
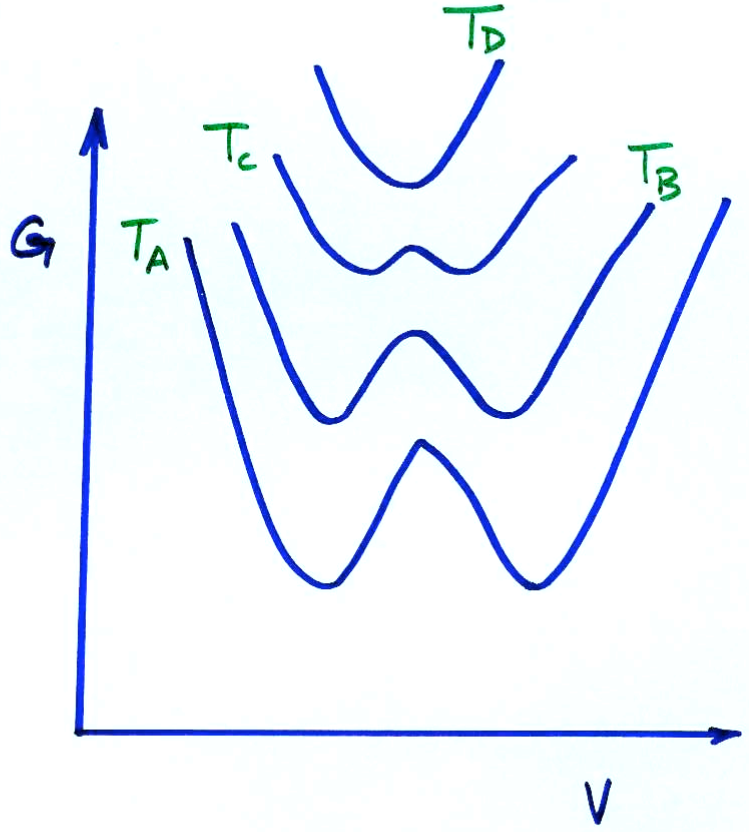


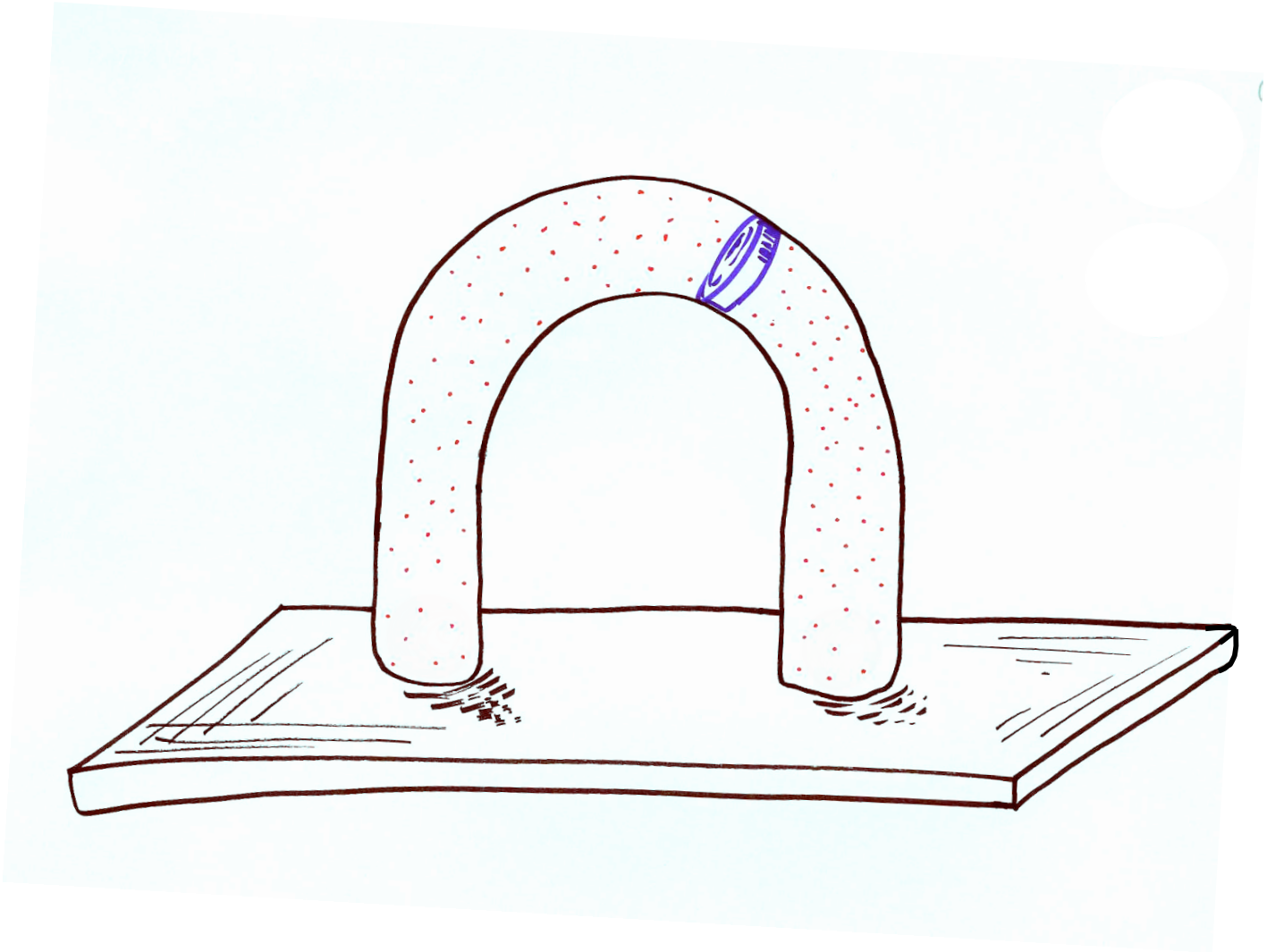

G (T, P, N)
V
T1
T2
T3
T4
T5
T1 < T2 < T3 < T4 < T5



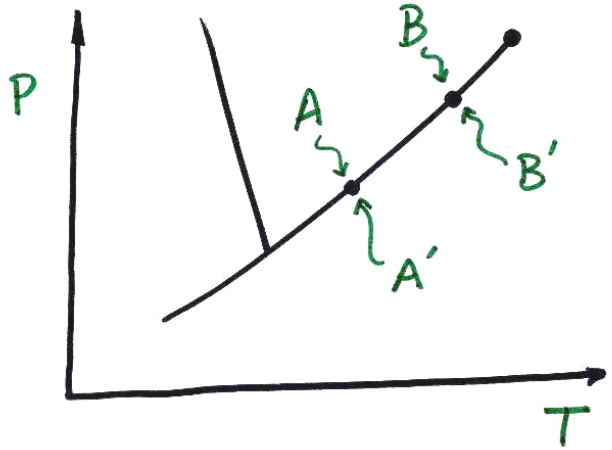


A,B,C: 1st ORDER

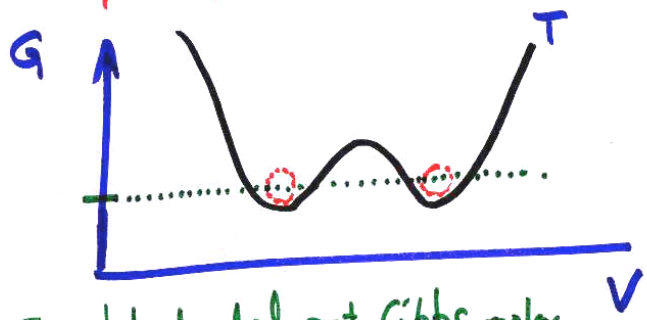
D: CRITICAL POINT
2nd ORDER



DISCONTINUIDADES



Si hay equilibrio de fases:



Igualdad del pot. Gibbs molar

$$\mu_A = \mu_{A'}$$
$$\mu_B = \mu_{B'}$$
$$\Big\} \quad \mu_B - \mu_A = \mu_{B'} - \mu_{A'}$$

1 mol

$$\mu_B - \mu_A = -S\,dT + V\,dP$$
$$\mu_{B'} - \mu_{A'} = -S'\,dT + V'\,dP$$
$$\Big\} \longrightarrow \frac{dP}{dT} = \frac{\Delta S}{\Delta V} = \frac{\ell}{T\Delta V}$$

Ec. de CLAPEIRON

CLASIFICACION TERMODINÁMICA

Como 1ª aproximación: (un tanto arcaica hoy)

- TRANSICIONES CON CALOR LATENTE $\ell \neq 0$
- TRANSICIONES SIN CALOR LATENTE $\ell = 0$

CLASIFICACION TERMODINÁMICA

Como 1ª aproximación: (un tanto arcaica hoy)

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P. Ehrenfest, 1933
Clasificación según potenciales termod.

→ 1er orden: discontinuidades en las 1as derivadas de los potenciales termodinámicos.

CLASIFICACION TERMODINÁMICA

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P. Ehrenfest, 1933
Clasificación según potenciales termod.

→ 1er orden: discontinuidades en las 1as derivadas de los potenciales termodinámicos.

ΔS $\qquad$ ΔV

$$S = -\left(\frac{\partial G}{\partial T}\right)_P \qquad V = \left(\frac{\partial G}{\partial P}\right)_T$$

$$\Delta S \neq 0 \Rightarrow \ell \neq 0$$

J. Phys.: Condens. Matter **11** (1999) 6969–6981. Printed in the UK PII: S0953-8984(99)95940-4

Metamagnetic transition and magnetocaloric effect in $ErCo_2$

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† Institute de Recherche sur l'Hydrogene, CP 500 Trois-Rivieres, Quebec, Canada G9A-5H7

‡ Max-Planck-Institut für Festkörperforschung, Heisenbergstraße 1, 70569 Stuttgart, Germany

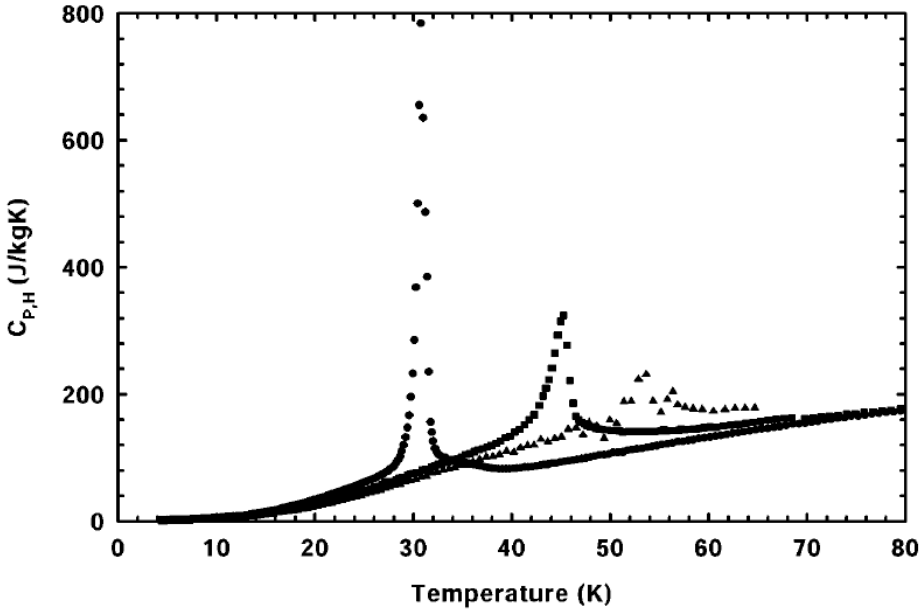


Figure 5. Temperature dependence of the specific heat capacity $c_{P,H}(T)$ in 0 T (●), 7 T (■), 14 T (▲) applied fields.

2º orden: TRANSICIONES EN LAS CUALES LOS POTENCIALES TERM. Y SUS 1as derivadas SON CONTINUOS PERO LAS 2AS (↑ ALGUNA(S)) DERIVADA(S) DIVERGEN ASINTÓTICAMENTE

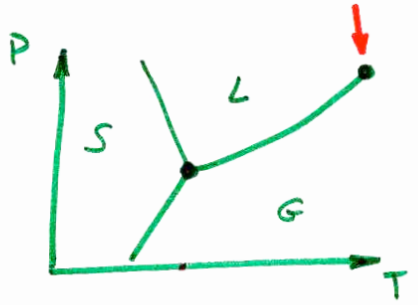
$$\frac{C_P}{T} = -\left(\frac{\partial^2 G}{\partial T^2}\right)_P = \left(\frac{\partial S}{\partial T}\right)_P$$

$$K_T V = -\left(\frac{\partial^2 G}{\partial P^2}\right)_T = -\left(\frac{\partial V}{\partial P}\right)_T$$

EN UNA TRANSICION DE 2º ORDEN:

- ~~∃~~ COEXISTENCIA DE FASES
- LAS "DOS FASES" SON LA MISMA EN EL PTO. CRÍTICO
- LA TRANSICIÓN ES CONTINUA

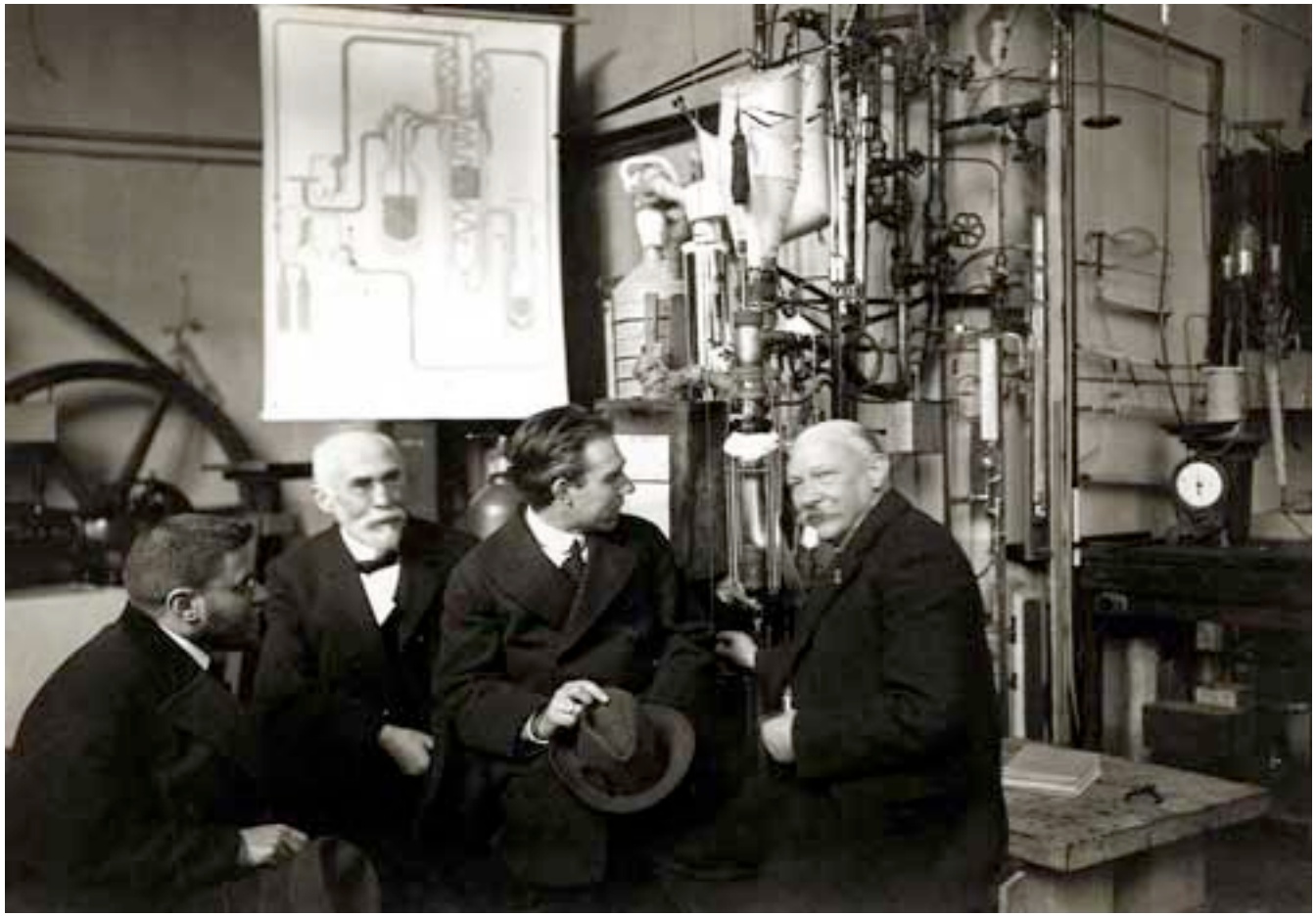
$\ell = 0 \Rightarrow$ T AUMENTA CONTINUAMENTE BAJO LA INYECCION DE Q



PUNTOS (o SUBESPACIOS) MULTICRITICOS

punto de orden p: coexisten p fases,

P. Ehrenfest



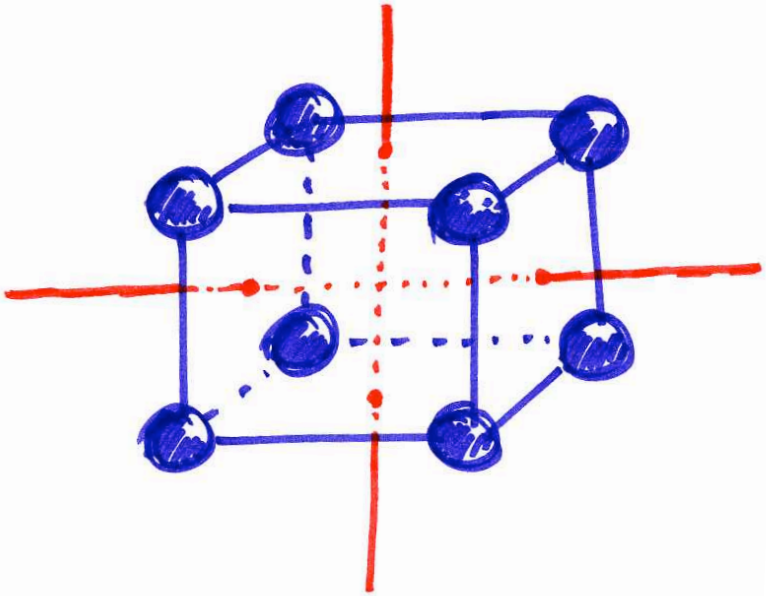
Paul Ehrenfest, Hendrik Lorentz, Niels Bohr, and Heike Kamerlingh Onnes (1919) in the Cryogenics Laboratory in Leiden

Ehrenfest's students, Leiden 1924. Left to right: Gerhard Heinrich Dieke, Samuel Abraham Goudsmit, Jan Tinbergen, Paul Ehrenfest, Ralph Kronig, and Enrico Fermi.

Clasificación de Landau

LANDAU, 1937

las transiciones con $\ell = 0$ se corresponden con la ROTURA DE ALGUNA SIMETRÍA



Clasificación de Landau

LANDAU, 1937

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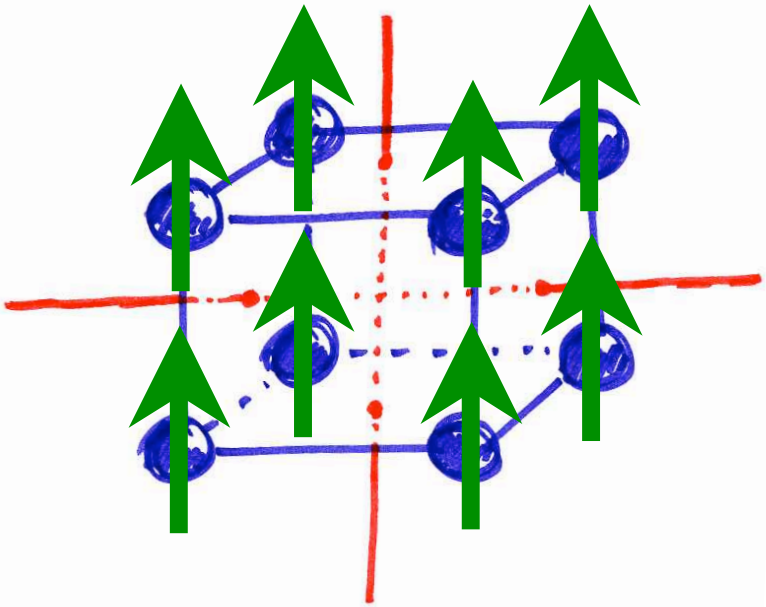

LANDAU, 1937

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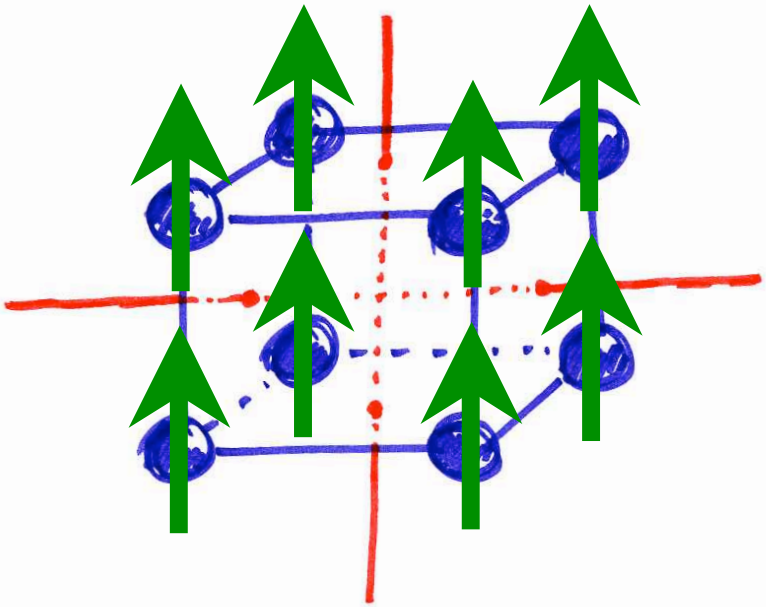
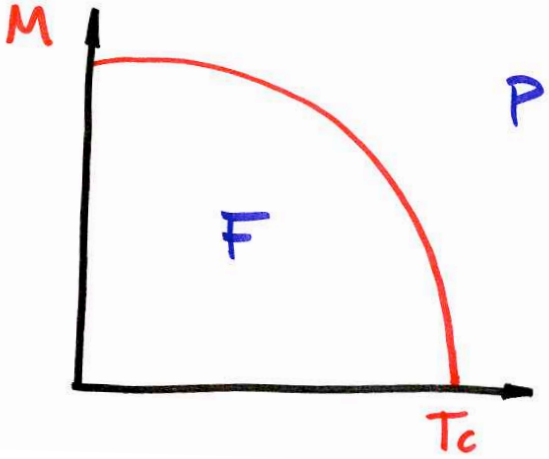


PERMITE DEFINIR UN PARAMETRO de ORDEN



TIPOS DE TRANSICIONES à la Landau

- TRANSICIONES SIN PARÁMETRO DE ORDEN

  GRUPOS DE SIMETRÍA DE AMBAS FASES NO SON UNO SUBGRUPO* DEL OTRO

  (SON SIEMPRE 1er ORDEN EN EL SENTIDO DE EHRENFEST: $\ell \neq 0$)

- TRANSICIONES CON PARÁMETRO DE ORDEN ϕ

$$G'_{\text{menos simétrica}} \subset G_{\text{más simétrica}}$$

ϕ { CONTINUO en T_c: $\ell = 0$

DISCONTINUO en T_c: $\ell \neq 0$

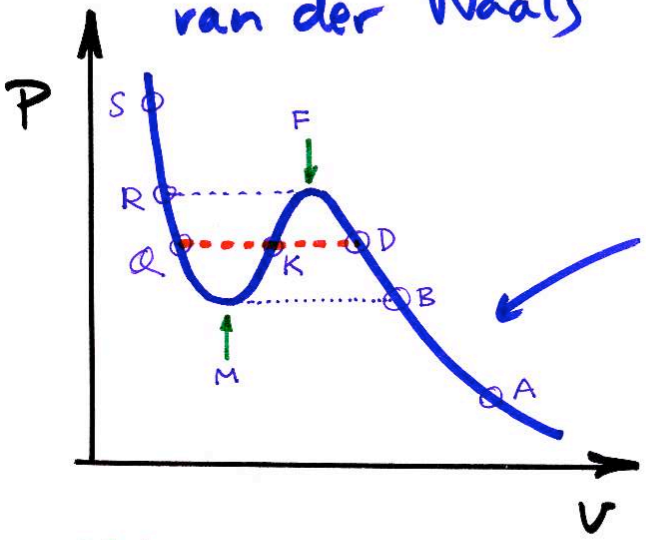
*ESTRICTO

Ecuación de van der Waals

ISOTERMAS INESTABLES

van der Waals

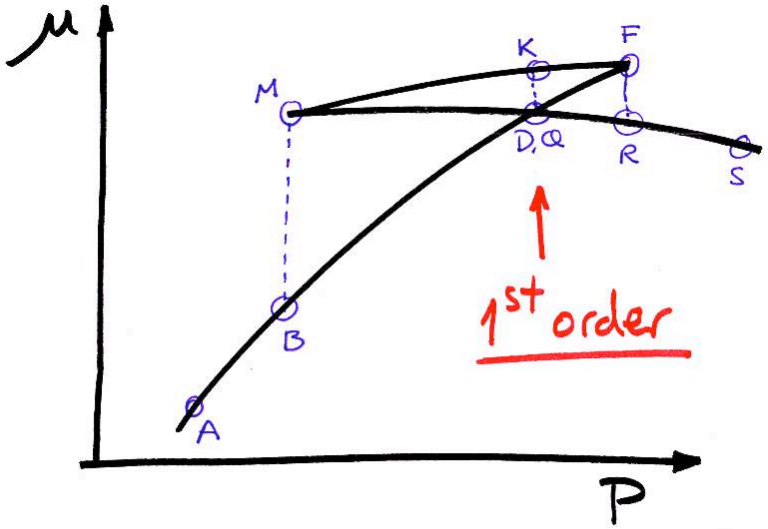
$$P = \frac{RT}{(v-b)} - \frac{a}{v^2}$$

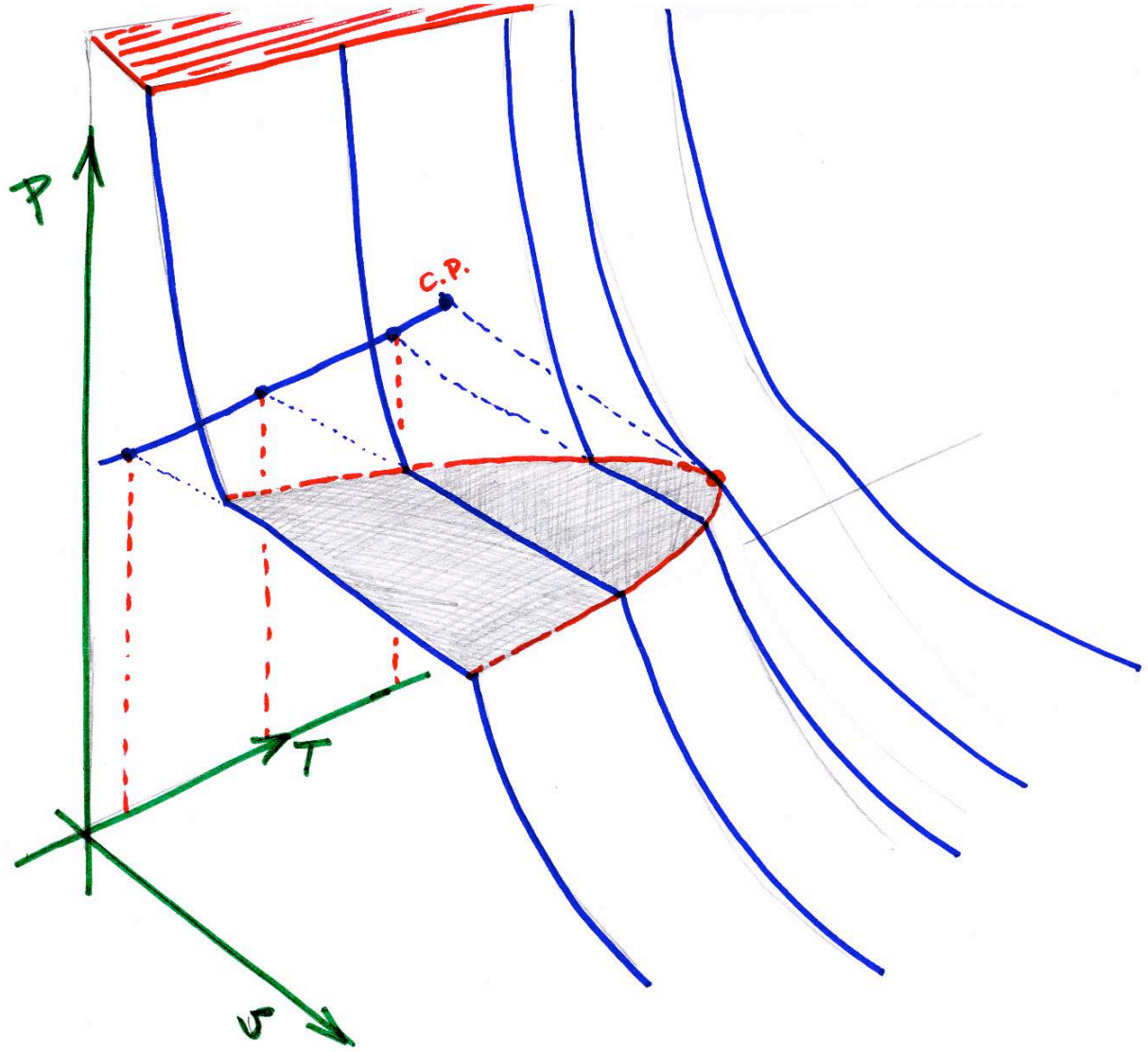


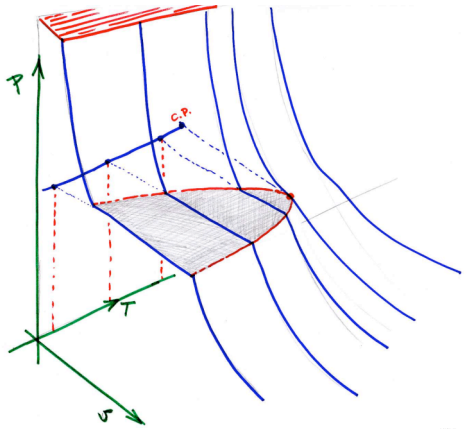
isoterma no estable si $\left(\frac{\partial P}{\partial v}\right)_T < 0$

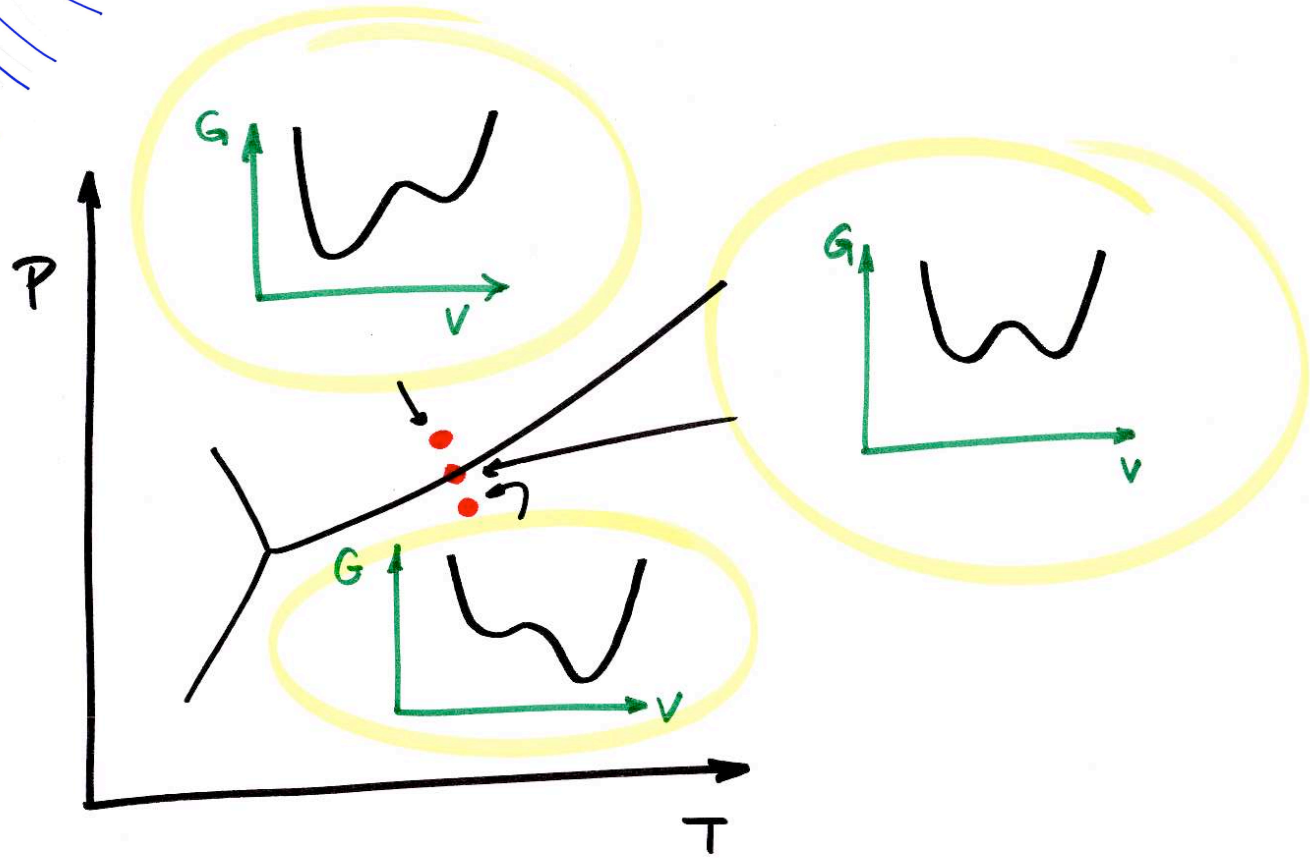
P(v) nos permite calcular $\mu = \int v\,dP + \phi(T)$

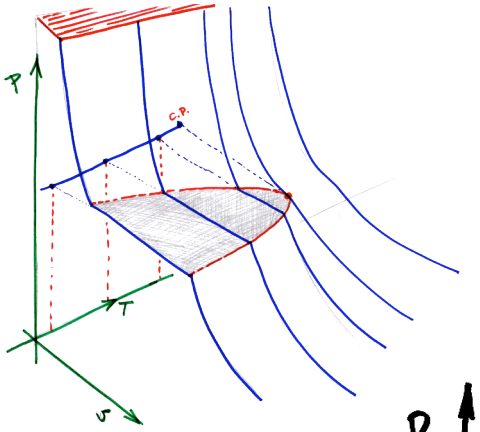
(porque $d\mu = -s\,dT + v\,dP$ GIBBS-DUHEM)

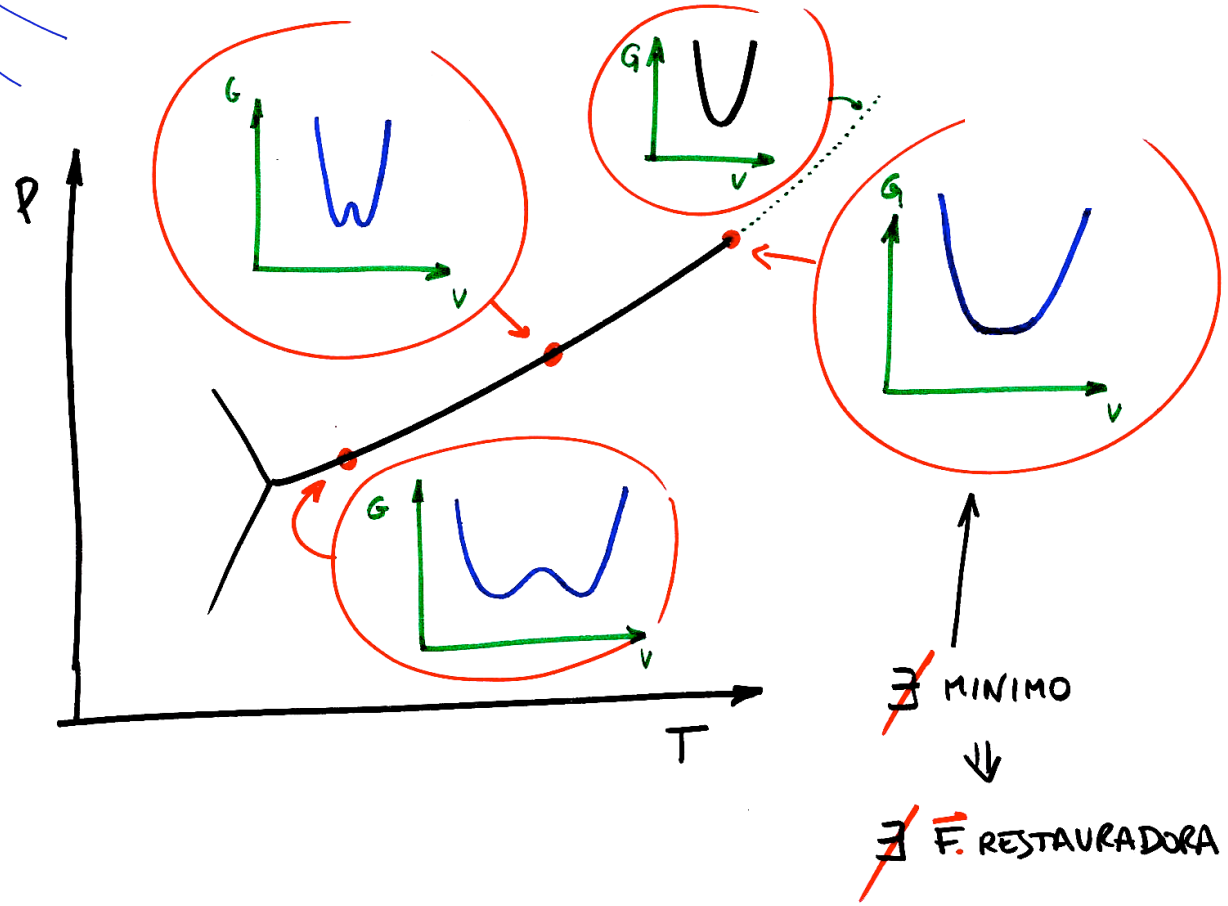



P
C.P.
T
V

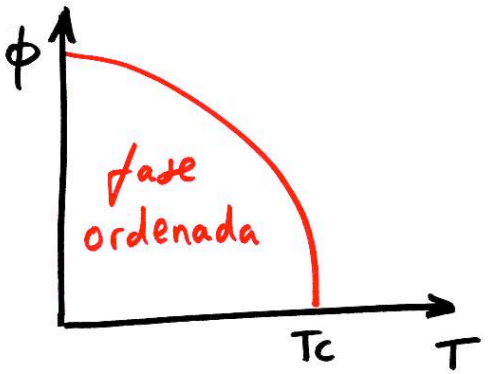

P
C.P.
T
S


G
V
P
T
G
V
G
V


P
C.P.
T
V


G
V
P
T
∃ MINIMO
∃ F. RESTAURADORA

TEORÍA DE LANDAU



GIBBS POTENTIAL ≡ $G = G(T, P, \phi, N_i)$

Cerca de T_c : ϕ es pequeño ⇒
se puede admitir el desarrollo

$$G = G_0 + G_1\phi + G_2\phi^2 + G_3\phi^3 + \dots$$

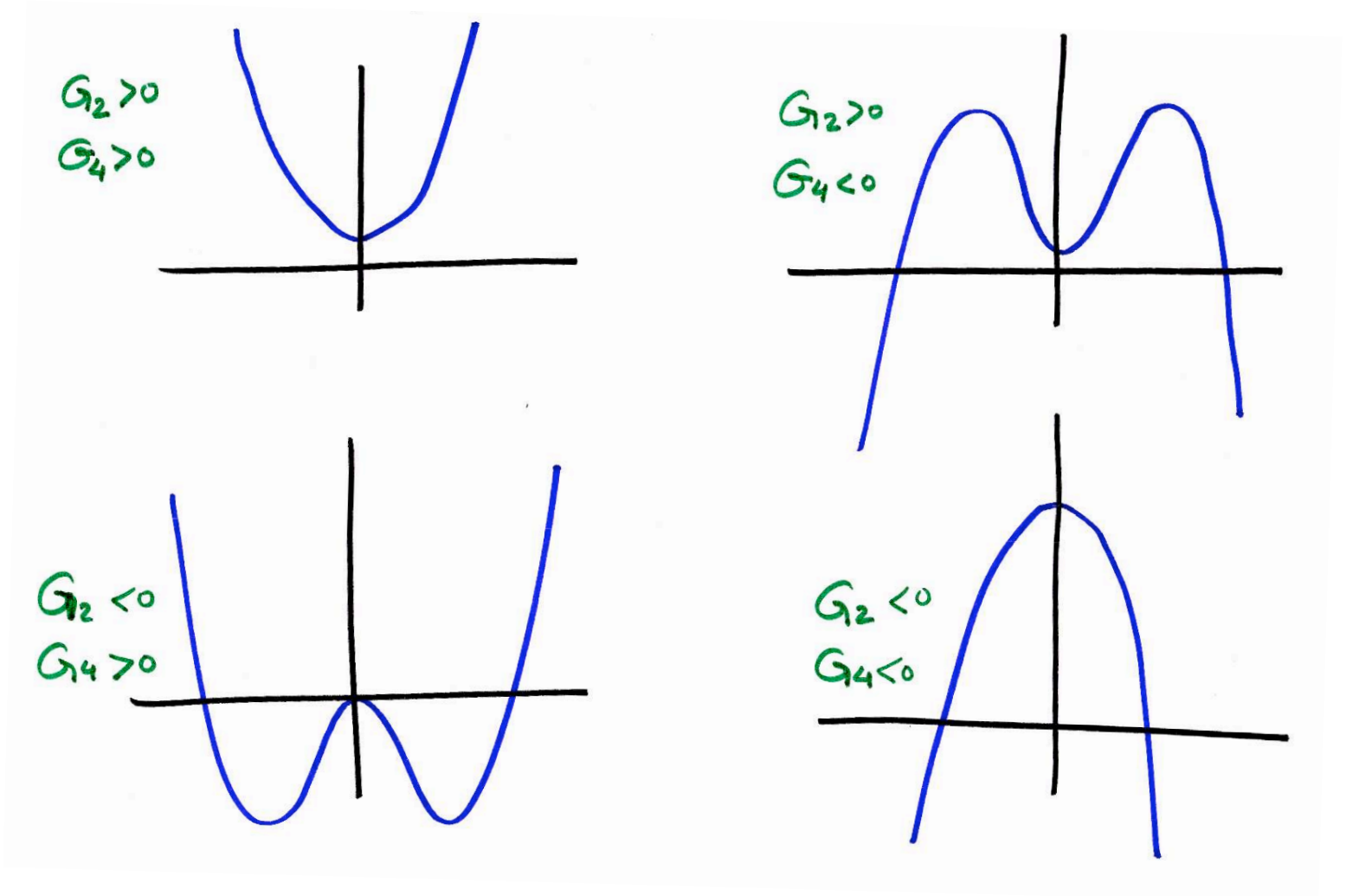
$$G_i = G_i(T, P, N_i)$$

En gral, G no debe depender del signo de ϕ $(\uparrow \text{ó} \downarrow)$

$\Rightarrow G_1, G_3, G_5 \dots = 0$

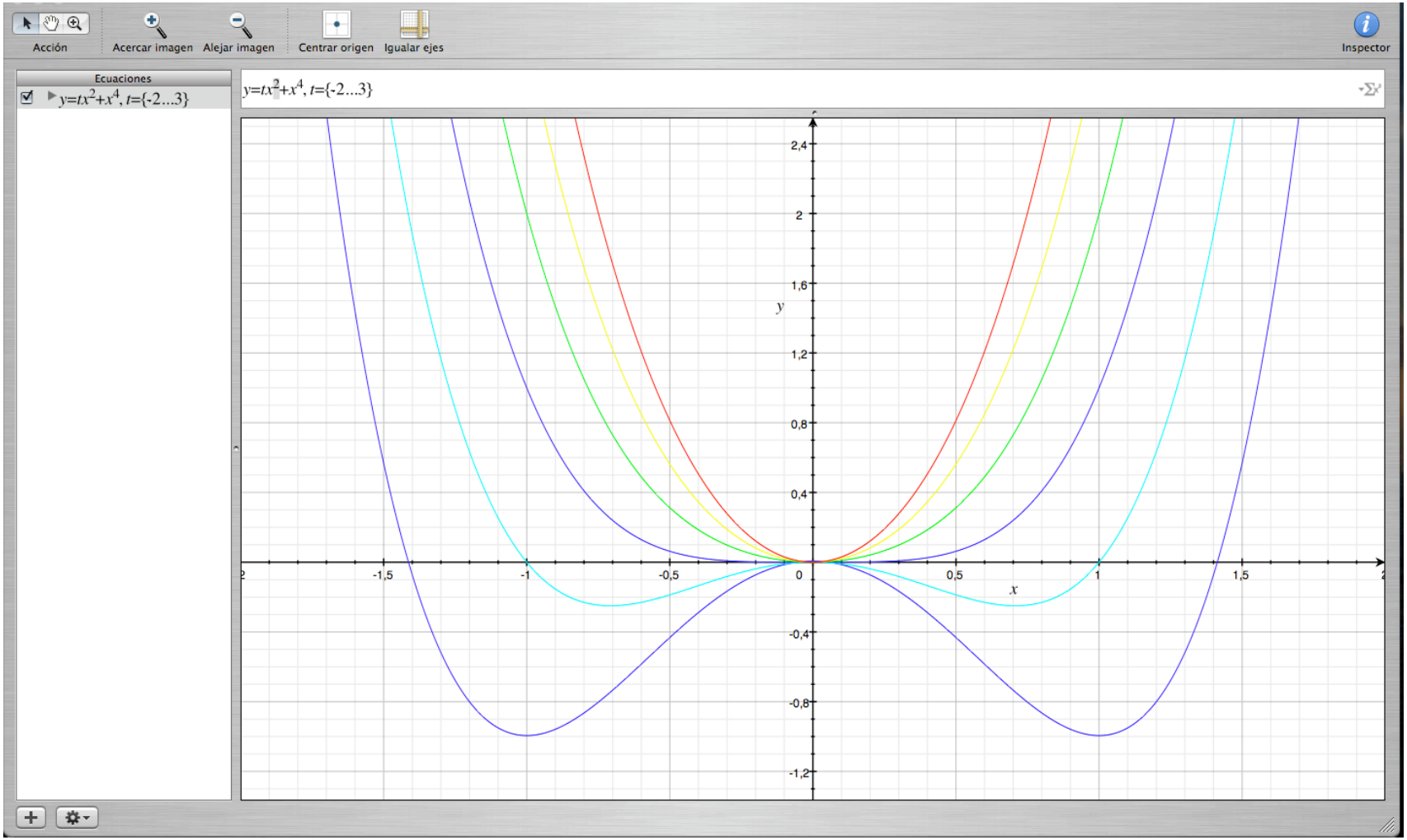
$$G = G_0 + G_2\phi^2 + G_4\phi^4 + \dots$$

$$G = G_0 + G_2\phi^2 + G_4\phi^4$$



Ecuaciones

$y=tx^2+x^4, t=\{-2...3\}$



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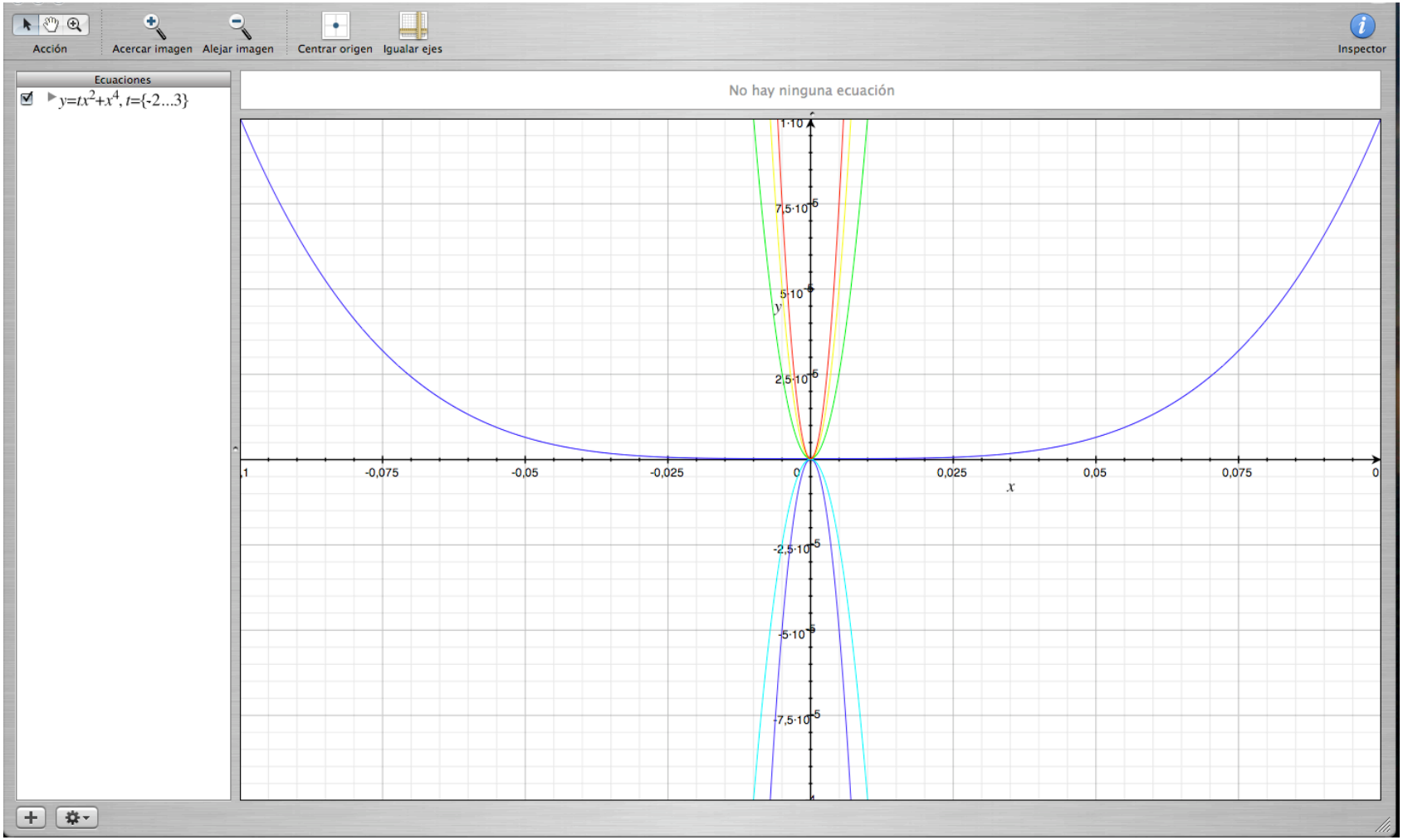

Punto crítico: $G_2 = 0$

por encima: $G_2 > 0$

por debajo: $G_2 < 0$

$\Rightarrow (T - T_c) G_2^0 + \mathcal{O}((T-T_c)^2)$

expandimos G_2 en f. de $(T - T_c)$

$G_2^0 = \left.\frac{\partial G_2}{\partial T}\right|_{T=T_c}$

la variación de ϕ con T en $T \approx T_c$ se determina con:

$$\frac{\partial G}{\partial \phi} = \phi\left(2G_2 + 4G_4\phi^2\right) = 0 \Rightarrow \phi\left(G_2 + 2G_4\phi^2\right) = 0$$

Si $\phi = 0 \longrightarrow$ solución "paramagnética" (NO ORDENADA)

Si $\phi \neq 0 \longrightarrow \phi^2 = -\frac{G_2}{2G_4} = \frac{G_2^0}{2G_4}(T - T_c)$

Obsérvese que si $G_2 < 0$; $\phi = 0$ es un máximo

ENTROPÍA:

$$S = -\frac{\partial G}{\partial T} = -\frac{\partial G_0}{\partial T} - \frac{\partial G_2}{\partial T}\phi^2$$

$\frac{\partial \phi}{\partial T}$ no cuenta pues $\frac{\partial G}{\partial \phi} = 0$!!

FASE "PARA" $\phi = 0$; $S = \frac{-\partial G_0}{\partial T} \equiv S_0$

FASE "ORDENADA" $\phi \neq 0$; $\phi^2 = -\frac{G_2}{2G_4} \Rightarrow S = S_0 + \frac{G_2}{2G_4} \cdot \frac{\partial G_2}{\partial T} =$

$$= S_0 + \frac{G_2^0}{2G_4} \cdot G_2^0 (T - T_c) = S_0 + \frac{G_2^0}{2G_4}(T - T_c)$$

$T \to T_c \Rightarrow S \to S_0 \Rightarrow$ S es continua en $T_c \equiv$ 2° orden

Sin embargo; $C_p = T\left(\frac{\partial S}{\partial T}\right)_p$

FASE "PARA": $C_p = C_{p0} + \frac{G_2^0 T_c}{2 G_4}$

"ORDENADA":

FASE "PARA": $S = S_0 \Rightarrow C_p = C_{p0}$

$\Rightarrow \exists$ SALTO EN C_p

Problema: calcular κ_T en T_c; Δ?

α en T_c; Δ?

$T < T_c$: solucion $\phi \neq 0$ 2 real solutions:

$$\phi = \pm \left[2 \frac{G_2^0}{G_4} (T_c - T) \right]^{1/2} \quad ; \quad T < T_c$$

$$\beta = 1/2$$

expt: 0.3 ~ 0.4

- problema: exponente de la susceptibilidad ($\gamma = 1$)

Estudiemos un caso magnético:

$$\phi \equiv m = \frac{M_s(T)}{M_s(0)} : m(T)$$

$$G(m,T) = \vec{m}\,\vec{B} + G_0 + G_2 m^2 + G_4 m^4 + \dots$$

como antes $m \to 0$ cuando $T \to T_c$ por debajo;

y como hemos visto:
- $G_2 > 0 \Rightarrow$ $m=0$ es mínimo G en T_c
- $G_2 < 0$ hace $m=0$ máximo en T_c
- $G_4, G_6 \dots > 0$!! (estabilidad)

$$\frac{\partial G}{\partial m} = 0 \Rightarrow B = 2G_0(T-T_c)m + 4G_4(T)m^3 \dots$$

$$\Rightarrow \boxed{\frac{B}{m} = 2G_0(T-T_c) + 4G_4 m^2}$$

PHYSICAL REVIEW VOLUME 108, NUMBER 6 DECEMBER 15, 1957

Criterion for Ferromagnetism from Observations of Magnetic Isotherms*

ANTHONY ARROTT
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(Received July 2, 1957)

A criterion is proposed for determining the onset of ferromagnetism in a material as its temperature is lowered from a region in which the linearity of its magnetic moment *versus* field isotherm gives an indication of paramagnetism. Within the limits of validity of a molecular field treatment, the Curie temperature is shown to be in general indicated by the third power of the magnetization being proportional to the internal magnetic field. The method has been employed to redetermine the Curie point of nickel from the data of Weiss and Forrer, of Fe_3O_4 from the data of Smith and of some alloys from the data of Kaufmann and his collaborators and the author.

Though in this paper the demonstration is in terms of plots of M^3 *vs* H, in practice we plot H/M *vs* M^2 as this gives $1/\chi$ in the limit of zero field as the intercept on the H/M axis when extrapolated to $M^2=0$. Not only does the temperature at which $1/\chi$ goes to zero determine the Curie temperature but the slope of $1/\chi$ *vs* temperature gives a measure of the magnetic moment per atom

$$H = \epsilon M + AM^3 + BM^5 + \cdots,$$

$$\epsilon = [(T/T_c) - 1]a.$$

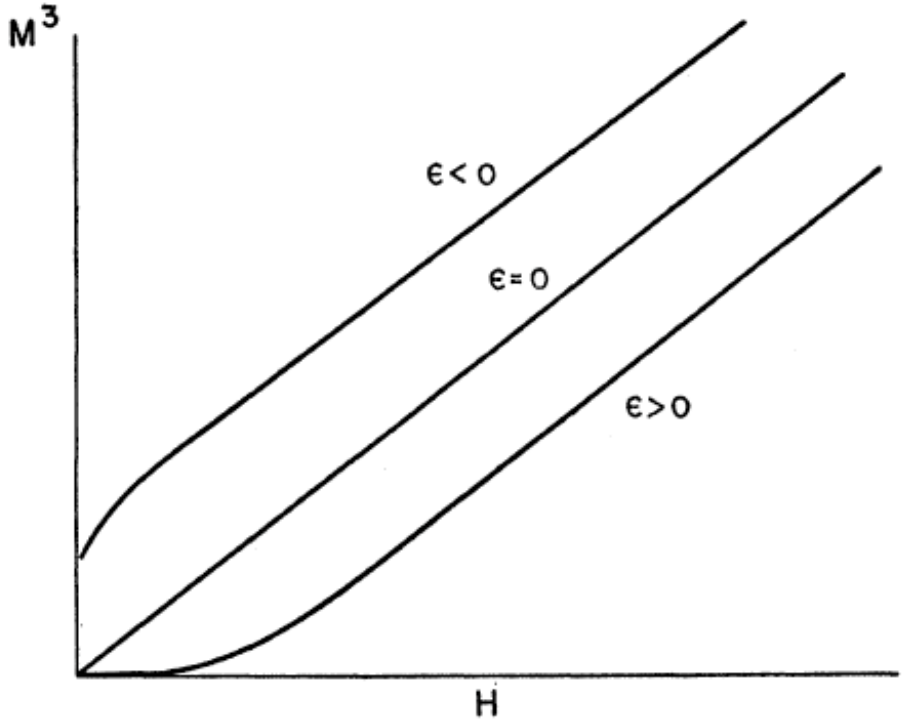
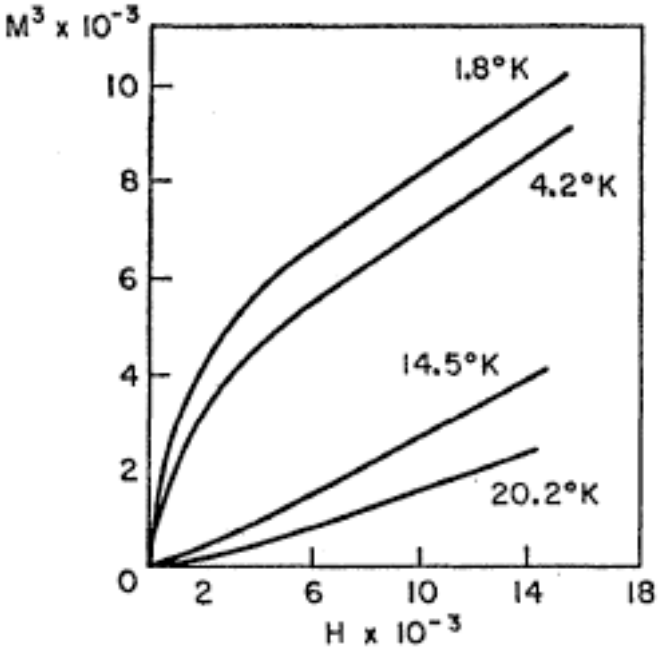


FIG. 1. Magnetization cubed *versus* field for temperatures just below the Curie point ($\epsilon<0$), at the Curie point ($\epsilon=0$), and just above the Curie point ($\epsilon>0$).

B. Some Applications to Existing Data

The application of this criterion to some data of the author is shown in Fig. 2. In this case the copper-nickel alloy in question is in the critical range of the transition from ferromagnetism to nonferromagnetism as a function of composition. The strong curvature in the plots of M *vs* H is suggestive of ferromagnetism at all four temperatures shown. Measurements were carried out on these samples in applied fields as low as 20 oe which showed a magnetization did exist in zero internal field for 1.8°K and 4.2°K but not for 14.5°K and 20.2°K. The plot of M^3 *vs* H shows agreement that the Curie point lies between 4.2°K and 14.5°K. Using an M^2 *vs* H/M plot to obtain $1/\chi$ and then extrapolating $1/\chi$ *vs* T gives the Curie point near 11°K.



PHYSICAL REVIEW VOLUME 126, NUMBER 1 APRIL 1, 1962

Magnetic Disorder as a First-Order Phase Transformation

C. P. Bean and D. S. Rodbell
General Electric Research Laboratory, Schenectady, New York

(Received November 10, 1961)

INTRODUCTION

As a ferromagnet is heated, the magnetization usually decreases in a continuous manner and vanishes at the Curie temperature. This behavior indicates that the change of phase from ferromagnetism to paramagnetism at the Curie temperature is not a first-order phase transition in as much as the entropy (which is monotonically and continuously related to the magnetization) suffers no discontinuous change. Indeed the Weiss molecular field theory of ferromagnetism gave the first analytic treatment of a second-order phase transition.

It is of interest to inquire whether or not it is possible for this transition to be one of first order.

$$T_c = T_0[1+\beta(v-v_0)/v_0],$$

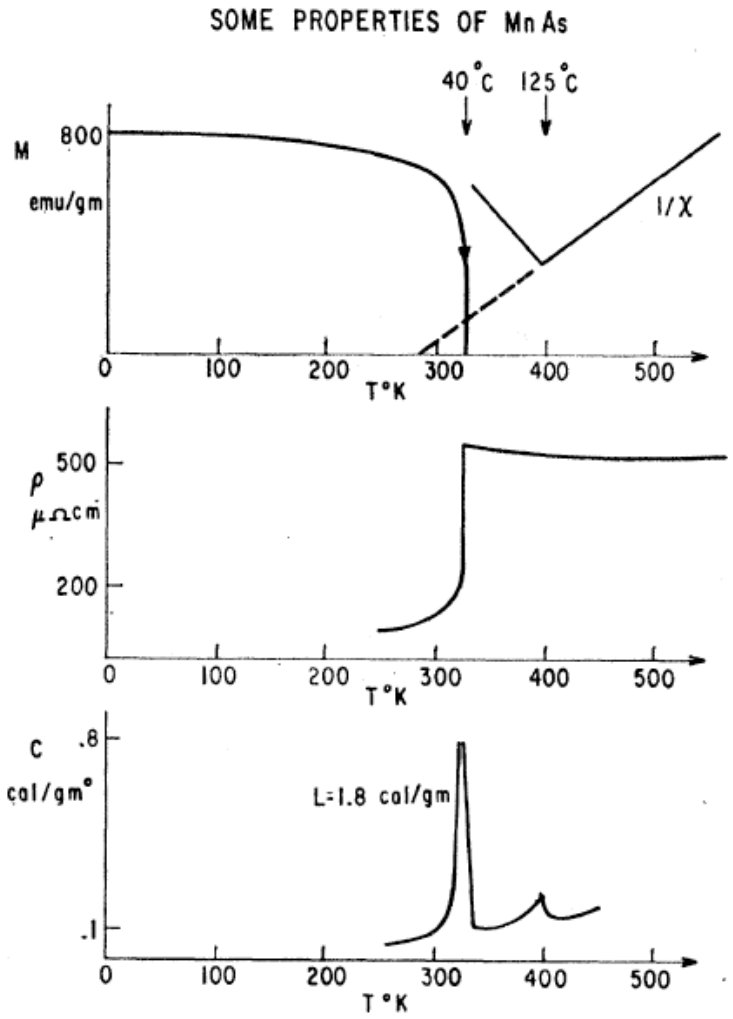


FIG. 1. Some features of the first-order phase transition exhibited by the compound MnAs.

stoichiometric compound MnAs. As has been known for many years,[1–8] this compound exhibits a discontinuous loss of ferromagnetism just above room temperature (see Fig. 1), and associated with this transition there is a latent heat of 1.79 cal/gm.[3] Early examination[5–7] had concluded that there was no change of crystal symmetry at this transition[9] although there is the discontinuous change of lattice parameter (i.e.,

Now let us consider what results if we assume that the exchange energy (or Curie temperature) is a strong function of interatomic spacing. We show such a dependence in Fig. 2(a) in the form of an exchange that depends on atomic volume. At absolute zero the system's free energy may be lowered by a distortion of the lattice in the direction of increasing the Curie temperature. The distortion will introduce to the free

The Gibbs free energy per unit volume is, within the molecular field approximation,

$$G_v = -HM_s\sigma - NkT_c\sigma^2/2 + (1/2K)[(v-v_0)/v_0]^2 + P(v-v_0)/v_0 - TNk[\ln 2 - \tfrac{1}{2}\ln(1-\sigma^2) - \sigma \tanh^{-1}\sigma], \quad (2)$$

where the first term on the right is the field term; the second, exchange; the third, distortion; the fourth, pressure; and the last, entropy. In (2), H is the applied magnetic field, M_s the saturation magnetization, σ the relative magnetization, N the number of particles per unit volume for volume v_0, k is the Boltzmann constant, and K is the compressibility. P and T are the pressure and temperature, respectively. The entropy of the spin system is obtained by the straightforward application of the Boltzmann definition of entropy.[12] We neglect other terms, in particular the entropy of the lattice,

$$(2G_v/NkT_0)_{\min} = -P^2K/NkT_0$$
$$-(2T/T_0)\ln 2 - 2HM_s\sigma/NkT_0$$
$$+[T/T_0 - 1 + PK\beta]\sigma^2 + \tfrac{1}{6}[T/T_0 - \eta]\sigma^4$$
$$+(T/15T_0)\sigma^6 + (T/28T_0)\sigma^8 + (T/45T_0)\sigma^{10} + \cdots. \quad (6)$$

The paramagnetic Curie point, as found previously (and again here), corresponds to the coefficient of the σ^2 term becoming zero, i.e., Eq. (5). The transition will occur at this temperature and be second order provided that the coefficient of the σ^4 term is positive, i.e.,

$$T_c/T_0 > \eta. \quad (7)$$

This last condition is necessary because otherwise at temperatures above T_c the negative σ^4 contribution leads to a minimum energy at $\sigma \neq 0$ and gives rise to the first-order transition indicated previously.

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ON A GENERALISED APPROACH TO FIRST AND SECOND ORDER MAGNETIC TRANSITIONS

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Landau [1] and Lifshitz [2] developed the thermodynamic theory of second order phase transitions. They showed that near the transition point, where the order parameter (J) can assume infinitely small values, the thermodynamic potential Φ can be expanded in a Taylor series. Thus

$$\Phi(T, P, J) = \Phi_0 + aJ^2 + bJ^4 + \dots , \qquad (1)$$

where the coefficients a and b are functions of the pressure (P) and the temperature (T), and Φ_0 is a constant. An equilibrium state is observed for the system when $\partial\Phi/\partial J = 0$. Vonsovskii [3] and Ginzburg [4] have successfully applied the above theory for the Curie point transitions in ferromagnets, where $J = J_T/J_0$. J_T and J_0 are spontaneous magnetisations per unit mass at temperatures T°K and 0°K respectively. In Ginzburg's formulation the magnetostatic field energy is also included, yielding

$$\Phi = \Phi_0 + aJ^2 + bJ^4 - JH \qquad (2)$$

Limiting the expansion to J^4. At equilibrium near the Curie point, the above reduces to

$$\alpha\sigma + \beta\sigma^3 = H , \qquad (3)$$

where α, β = constants incorporating a, b and J_0 and σ = experimentally observed specific magnetisation.

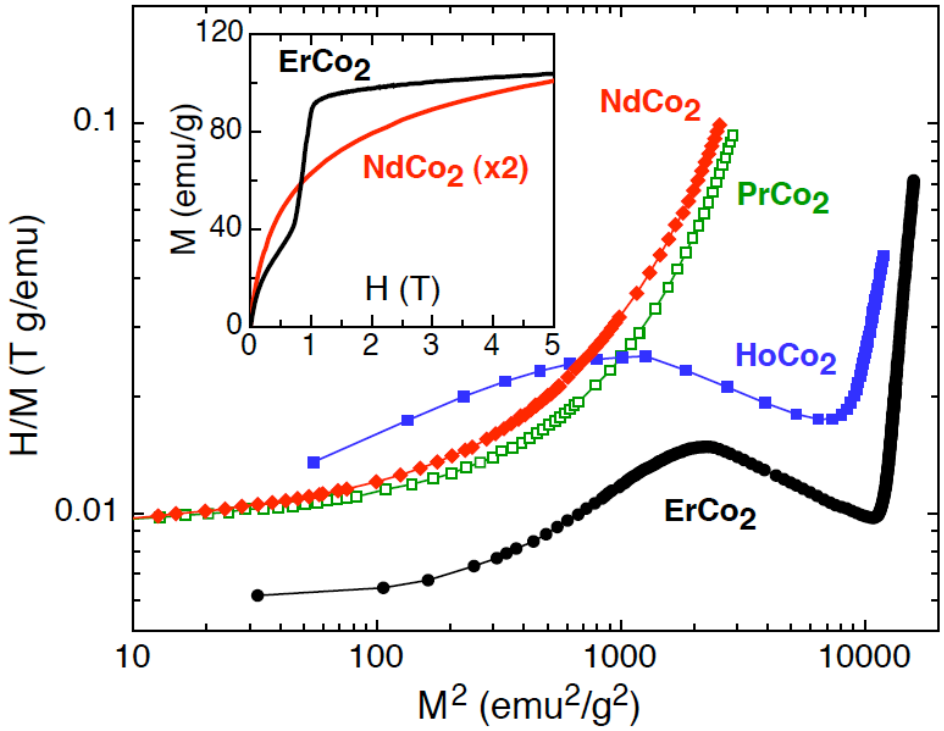

FIG. 2: Double-log H/M vs. M^2 plot of isotherms of $NdCo_2$, $PrCo_2$, $ErCo_2$, and $HoCo_2$ measured at temperatures slightly above $T_C^{H=0}$. Only the FOTs do show a negative slope section. The inset shows the magnetization curves of $ErCo_2$ and $NdCo_2$ (which has been multiplied by a factor of 2 for clarity).

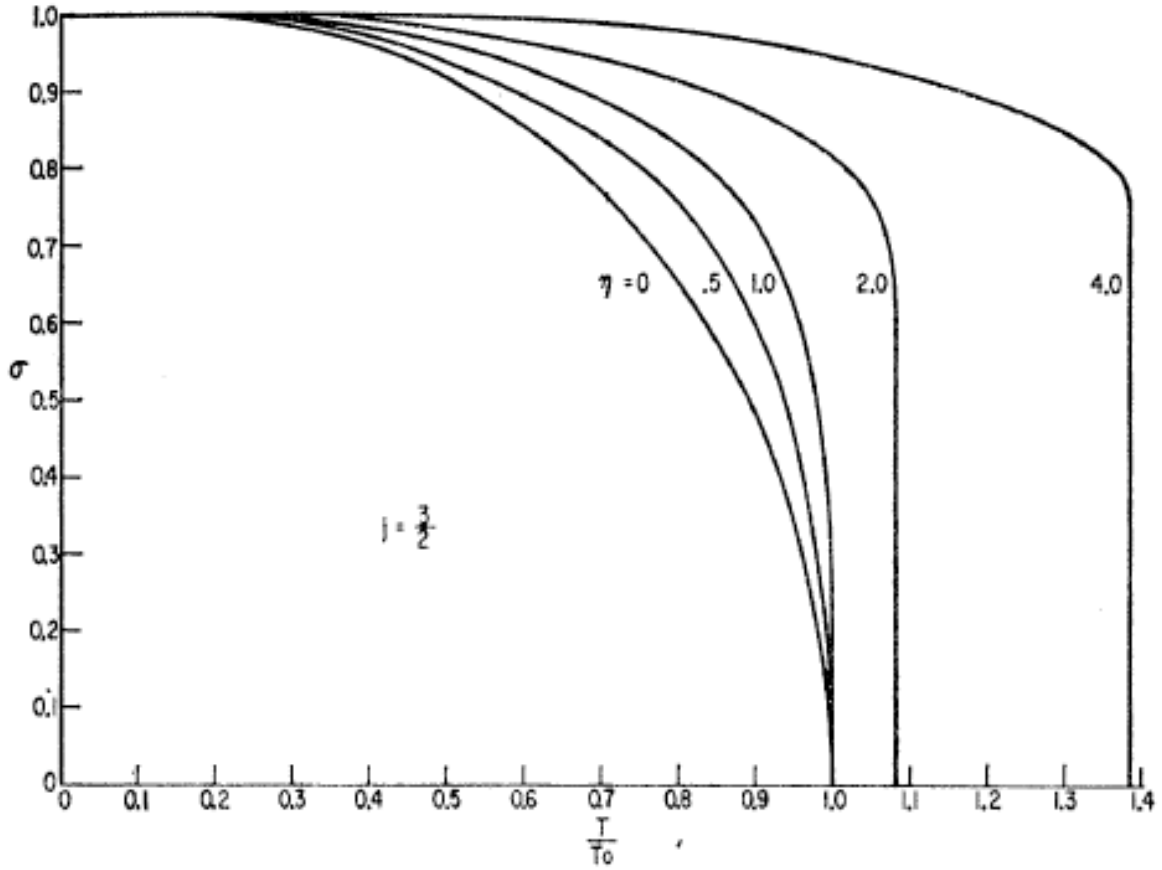

FIG. 16. The theoretical course of the magnetization vs the temperature for a $j = \frac{3}{2}$ spin system and evaluated for the indicated values of η.

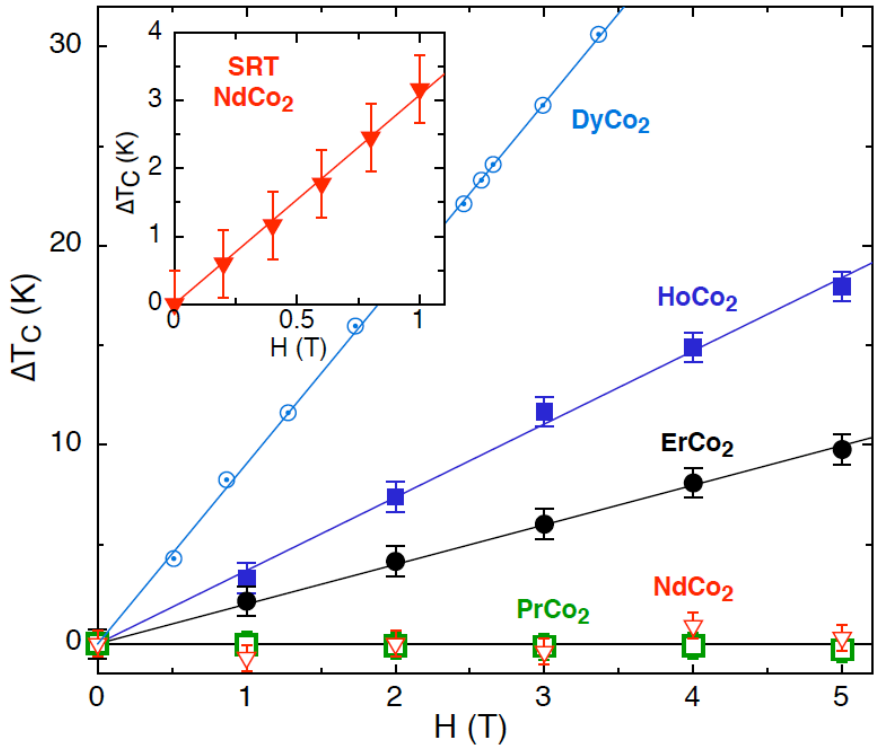

FIG. 1: Variation of the critical temperature with the applied magnetic field in the RCo_2 series. The inset shows data for the spin reorientation transition in $NdCo_2$.

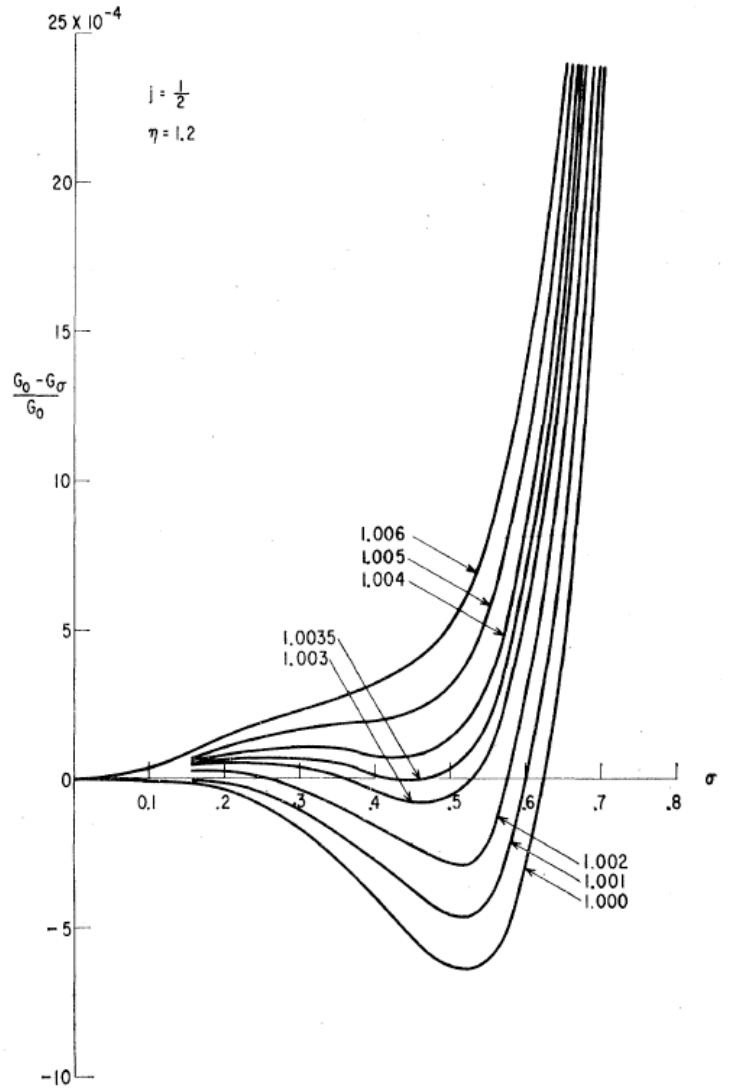

FIG. 4. The free energy isotherms in the vicinity of T_0 for a spin $\frac{1}{2}$ system characterized by $\eta=1.2$; the curve indices are the ratio T/T_0.

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Identification of first- and second-order magnetic phase transitions in ferromagnetic perovskites

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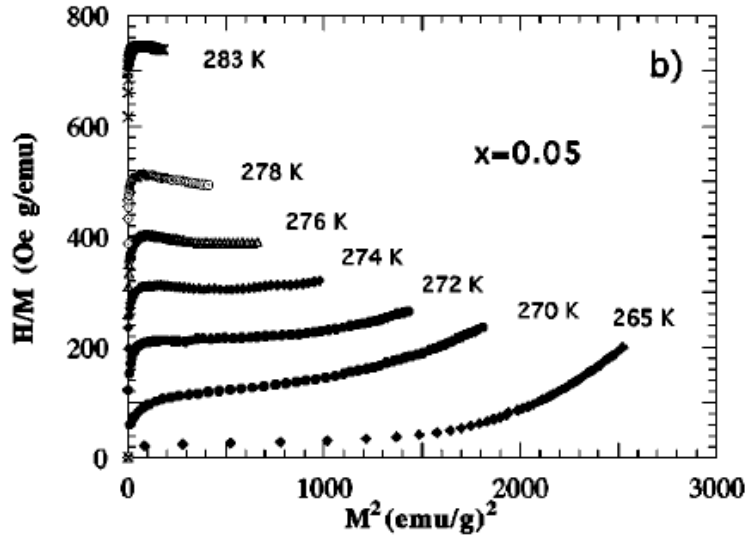
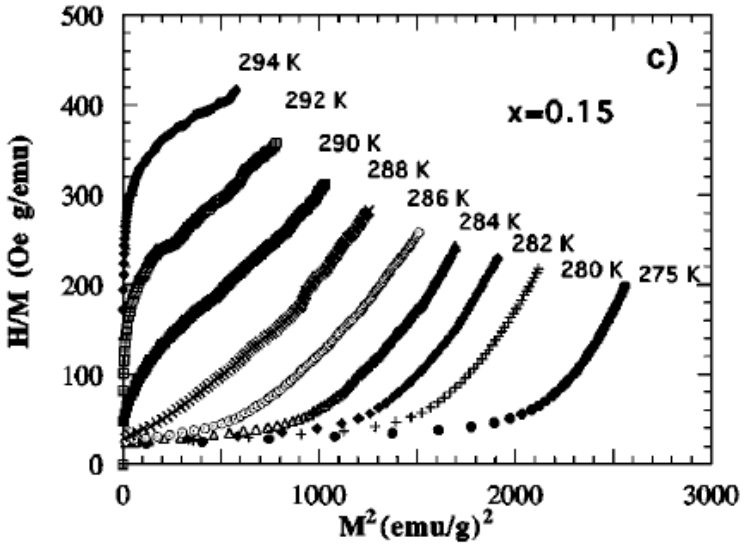
Abstract

A criterion used for the determination of first- and second-order magnetic phase transitions from purely magnetic methods is applied to manganese perovskites of formula $La_{2/3}(Ca_{1-x}Sr_x)_{1/3}MnO_3$. A crossover from first- to second-order character at a tolerance factor $t = 0.92$ is found, which also brings about several variations in other physical properties. At $t = 0.92$ a change from orthorhombic to rhombohedral symmetry also takes place. The impossibility of establishing static cooperative Jahn–Teller distortions in the rhombohedral symmetry is suggested as being responsible for the observed behaviour.

Keywords: Manganites; Phase transitions; Jahn–Teller distortions

Criterio de Banerjee





RCo_2: DSC

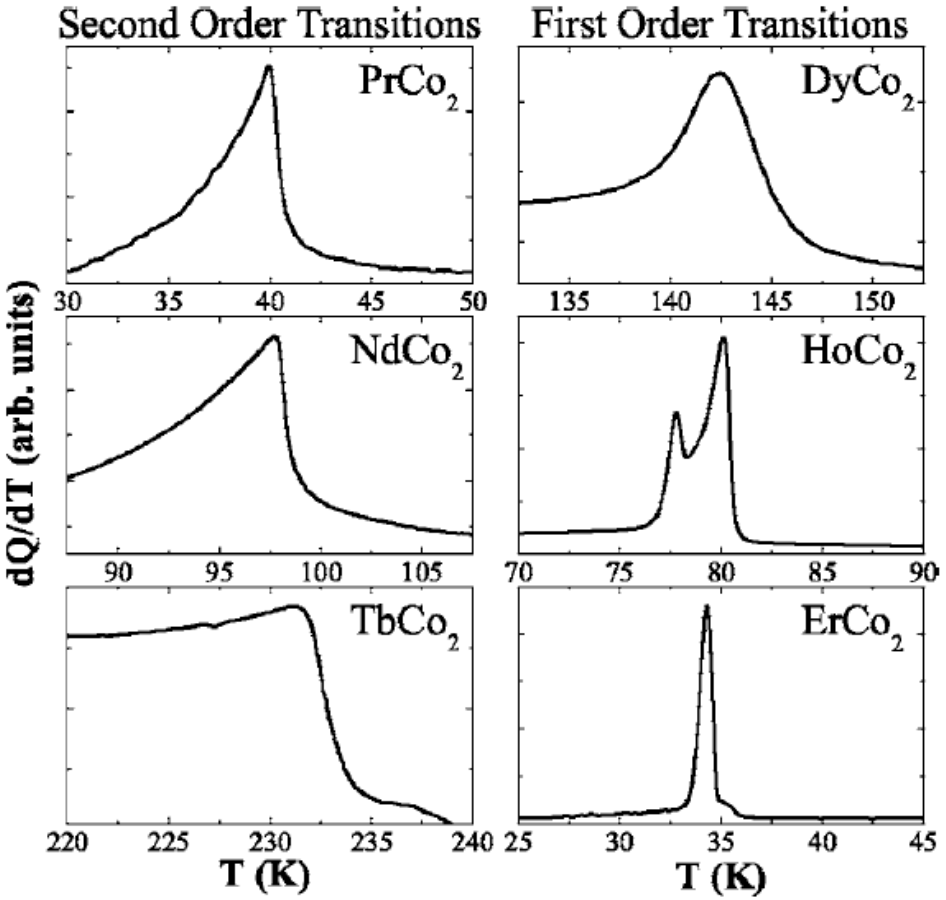
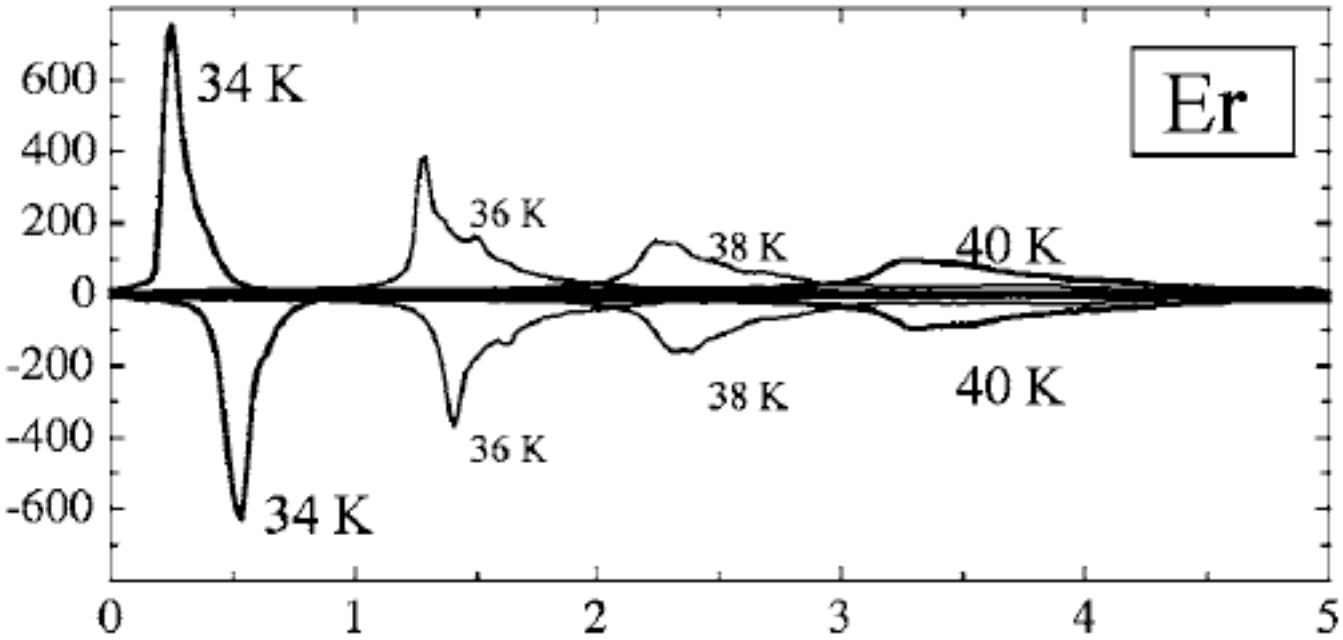


FIG. 3. DSC heating runs at zero field for RCo_2 (R=Pr, Nd, Tb, Dy, Ho, and Er).

RCo_2: DSC


Er
34 K
36 K
38 K
40 K
38 K
40 K
36 K
34 K
600
400
200
0
-200
-400
-600
0
1
2
3
4
5

RCo_2 : ΔS

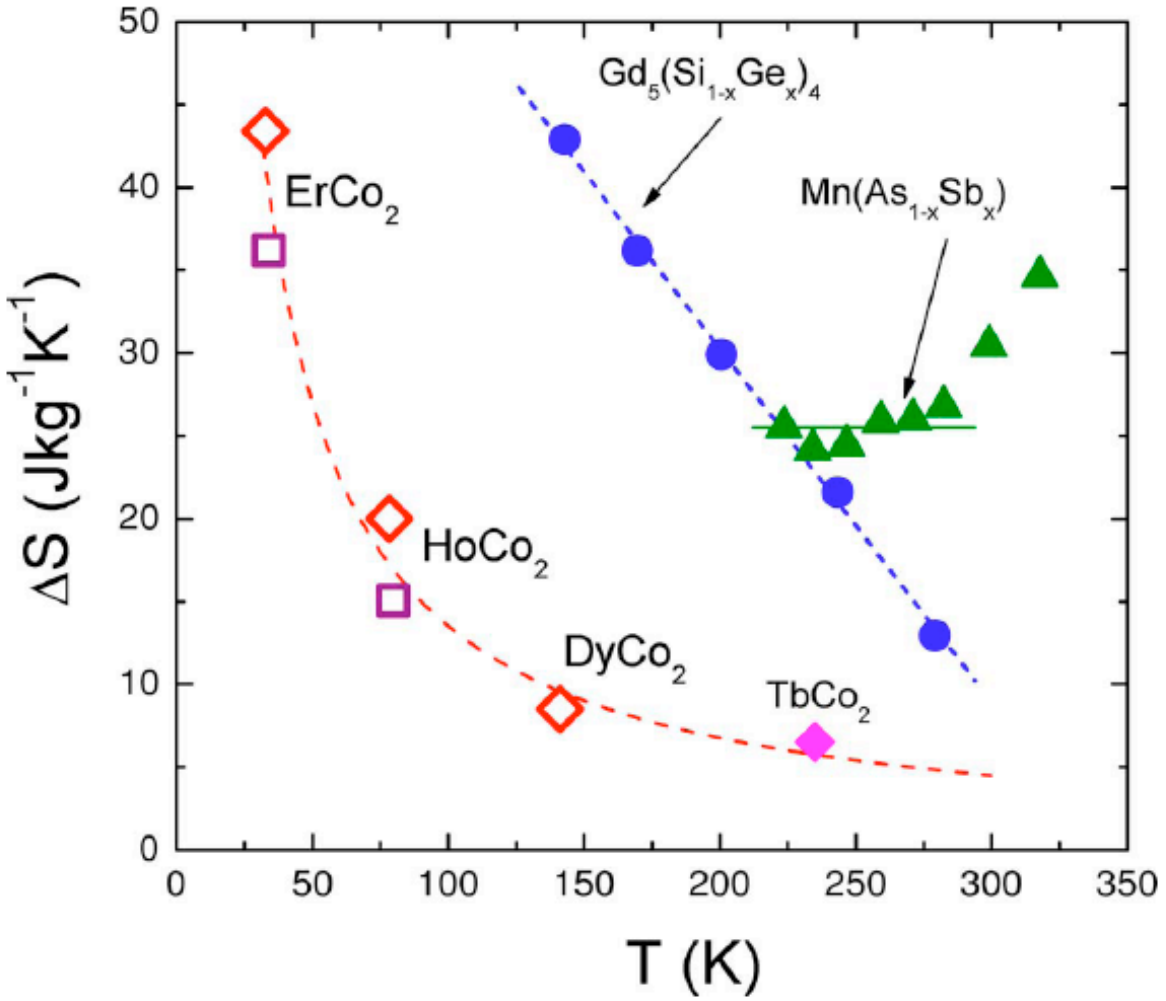


FIG. 9. (Color online) ΔS values as a function of critical temperature at the magnetostructural transitions of some magnetocaloric compounds.