On the scaling of the \((H,T)\)-phase diagram of \(\text{CuGeO}_3\).

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The \(H-T\) phase diagram of \(\text{CuGeO}_3\) has been determined, for different values of the hydrostatic pressure, utilizing optical absorption spectroscopy on the \(\text{Cu}^{2+}\cdots d\cdots d\) transitions. It is shown that the intensity of the related zero phonon line transition is very sensitive to the local environment of \(\text{Cu}^{2+}\), allowing for precise determination of all phase transitions. It is found that the phase diagrams at various pressures do not scale according to the Cross-Fischer theory. An alternative scaling is proposed.

Since the discovery of the spin-Peierls (SP) transition in the inorganic compound \(\text{CuGeO}_3\)\textsuperscript{1} there has been an increasing experimental and theoretical interest for the physics related to low dimensional magnetism \textsuperscript{2}. One of the most characteristic properties of a spin-Peiers material is its magnetic field \((H)\)-temperature \((T)\) phase diagram (PD). For the quasi-one-dimensional \(\text{Cu}^{2+}\) spin system \(\text{CuGeO}_3\), this PD has been explored using a variety of techniques \textsuperscript{3,4}. The investigation using thermal expansion/magnetostriction measurements \textsuperscript{3} has shown that \(\text{CuGeO}_3\), which crystallizes into an orthorhombic structure \((a=0.481\ \text{nm},\ b=0.843\ \text{nm} \text{and} \ c=0.295\ \text{nm})\), exhibits more drastic changes along the \(a\) and \(b\) axis than along the \(c\)-axis (which bears the \(\text{Cu}^{2+}\) ions) at all lines describing the PD. This underlines the importance of the elastic energies involved in these transitions.

From a theoretical point of view the corresponding PD is believed to be universal \textsuperscript{5,6} defining in the \(H-T\) plane a high temperature uniform phase (U) and a dimerized (D) phase below \(T_{sp}\) and magnetic fields below a critical value \(H_c\) \((T_{sp}\approx 14\ \text{K} \text{and} \ H_c\approx 13\ \text{T} \text{for} \ \text{CuGeO}_3)\). Above \(H_c\) and at low temperatures the system enters an incommensurate solitonic magnetic phase (I) which evolves into a sinusoidally modulated phase for higher fields \textsuperscript{7}. The best established theory for spin-Peiers materials is the one due to Cross and Fisher (CF) \textsuperscript{7,8}. Apart from the universality of the PD, one of the main theoretical results is that, at low \(H\) values the transition temperature scales with the square of the field. For \(\text{CuGeO}_3\) this scaling requires a further reduction of \(H\) by 10\% \textsuperscript{9}. The universal character could be eventually the consequence of approximations made in the model and since to our knowledge there is no complete experimental study of this aspect, the question deserves a careful inspection.

In order to achieve this goal one has to vary \(T_{sp}\). When accomplished by chemical substitutions \textsuperscript{10,11}, the question of the relative quality and purity of samples becomes acute. A more appropriate way is to apply, on a given sample, hydrostatic pressure which increases \(T_{sp}\) in \(\text{CuGeO}_3\) \textsuperscript{11,12}. It has been argued that this increase results from an increasing frustration in the spin system under pressure \textsuperscript{13}. This, in turn, gives an additional interest for the study of the PD under pressure. Technically speaking the standard techniques to measure the PD are not easy to settle in a high pressure cell. We have therefore decided to adopt an optical technique which has been shown recently to demonstrate around \(\hbar\omega = 1.47\ \text{eV}\) specific anomalies at the different phase transitions \textsuperscript{9,14}.

After a brief description of the technical aspects, we will first refine the analysis of the optical data trying to explain what is indeed measured and how it can be interpreted. The second part of this Letter presents and discusses the results obtained with this technique under high pressure.

The crystals of \(\text{CuGeO}_3\) used in this study have been grown by a traveling floating zone technique \textsuperscript{12} and cleaved in such a way the surface of the sample contains the \(c\) and \(b\)-axis. The absorption measurements in the visible region around 1.47 eV have been done on samples with a thickness \(d=2\ \text{mm}\) using a standard optical set-up. Magnetic fields \(H\) up to 23 T were provided by a modified resistive Bitter magnet and applied parallel to the \(a\)-axis of the sample. The high pressure measurements were made in a small piston high pressure cell filled with a mixture of ethanol-methanol, equipped with two sapphire windows to perform transmission measurements. The temperature was recorded with a cernox thermometer for which the magneto-resistance has been calibrated at different temperatures.

The optical technique consists \textsuperscript{16} in investigating the optical properties of \(\text{CuGeO}_3\) in the low energy tail of the intra-center absorption of the \(\text{Cu}^{2+}\)-ions. This absorption band, centered at \(E\approx 1.63\ \text{eV}\), has been analyzed carefully \textsuperscript{17}. It results in a broad band with a maximum absorption coefficient \(\alpha(E)\) ranging from 500 to 800 cm\(^{-1}\) (depending on the polarization), and shows that in the range of 1.47 eV the remaining absorption coefficient is expected to be less than 1 cm\(^{-1}\). In these conditions, the appropriate way to investigate optical properties is not by measuring reflection, which becomes a complicated function of reflectivity and transmission responses, but by direct transmission measurements. If one
performs such experiments, on wedged samples to avoid interference effects, the transmission $T$ is given by the standard expression

$$T(\hbar\omega) = \frac{(1 - R)^2 \exp(-\alpha(\hbar\omega)d)}{1 + R^2 \exp(-2\alpha(\hbar\omega)d)}$$

where $R$ is the reflectivity coefficient of one interface. For low absorbing media $R$ reduces to $(n-1)^2/(n+1)^2$, where $n$ is the refractive index ($\sim 2.5$ for CuGeO$_3$ [3]), implying $R \approx 0.13$. In such conditions, when measuring the ratio of the transmission coefficient with respect to that of a reference point ($T_0$), the denominator of Eq. 1 can be approximated to 1. Furthermore, since $R$ is not expected to vary significantly neither with $T$ nor $H$ one arrives at

$$T/T_0 = \exp(-\alpha d(\hbar\omega)) = \exp(-\Delta\alpha d),$$

where all optical functions are dependent on the photon energy $\hbar\omega$. The absorption strength is strongly polarized [16,18], but all discontinuities related to the phase transitions are not dependent on this polarization [14]. Since it is not easy to perform polarized measurements in a high pressure cell, we report here on non-polarized measurements only. The relevant physical quantity is indeed $\Delta\alpha d = -\ln(T/T_0)$. A typical variation of this quantity at fixed temperature and different values of $H$ is presented in Fig. 1b. One sees a clear discontinuity of the intensity, corresponding to the first-order transition at the critical field $H_c$ as already reported [16]. We shall see below that this value corresponds quite well to $H_c$ values reported by other techniques.

Before detailing the main results one has to discuss the origin of the optical transition we are studying. In the picture of non-interacting ions the absorption occurs between vibronic transitions involving as the initial state an electron in the $d$ fundamental state and $m = 0$ vibrational state (at low $T$) and as the final state the electron in the $d^*$ excited state of the ion and $m = l$ phonons in a displaced configuration coordinate $Q_r$ with respect to the initial value $Q_0$. The system relaxes in the excited state, after absorption, towards a lower energy by emitting these $l$ phonons [20]. The strength of the optical matrix element is essentially governed by the overlap of the $m = 0$ phonon wave function and the displaced $l$ phonon wave function. For simple cases where only one type of phonons is involved one gets the picture sketched in Fig. 1a. Therefore one observes around 1.47 eV the so-called zero-phonon-line (ZPL) for which $l = 0$ and the energy is $E_{ZPL}$. Of course due to the coupling of the different Cu$^{2+}$ ions, one expects the corresponding transition be broadened and this is indeed observed since the width $\Gamma$ of the spectra is of the order of 10 meV and does not vary much with $T$ and $H$. Because this width remains much smaller than that of the absorption band ($\approx 0.5$ eV) [3] one may still apply, in a first approximation to our case, the results known for isolated centers. In this context the probability to absorb a photon in the $l$th vibronic state, neglecting the constant electronic part of the matrix element, is given by: $P(l) = \exp(-S)/l!$. $S$ is the number of phonons emitted after the absorption at $\bar{E}$ (Fig. 1a). The phonon involved in this process has been determined in Ref. 18 and corresponds very likely to the IR active phonon at $\hbar\omega_p = 28.5$ meV [21]. With that analysis one gets $S$ values of about 6 which correspond to a very strong electron-phonon interaction. This gives in turn a mean absorption coefficient of the ZPL of about 0.25 cm$^{-1}$ which justifies the transmission technique used here. In non-polarized experiments the situation is not simple because, if there exists a nice well-defined line for the electric field of the light $\vec{E} \parallel c$-axis, the situation for $\vec{E} \parallel b$-axis is more complex [14] and this explains the high energy shoulder of the spectra in Fig. 1b. Therefore $S$ has to be understood as an averaged value of the relaxation energy of the Cu$^{2+}$ ions in the excited state over the different relaxation routes. The total integrated quantity, $M_0(H,T) = \int_0^T \Delta\alpha dE$, has been evaluated over a fixed range of energies between 1.45 eV and 1.50 eV. If one knows $M_0$ at a reference point, which will be taken for each pressure at $T = 2$ K and $H = 0$ T, it is easy to show that the variation of $M_0$ mimics quite well that of $\Delta S = S(0, 2 K) - S(H, T)$ i.e. the variation of the relaxation energy with $H$ and/or $T$.

![FIG. 1. a) schematic configurational diagram for the intra-center absorption of the Cu$^{2+}$ ions; b) variation of $\Delta\alpha d$ at $P = 1$ bar, $T = 2$ K for different values of magnetic field increasing by steps of 2 T beyond 8 T.](image)
of these ions in the excited state. This is indeed observed since in that range of temperature $S$ is found to increase by a factor of about 2 corresponding to a decrease of the relaxation energy of about 57 meV.

Now that the nature of the 1.47 eV absorption feature in CuGeO$_3$ has been established, we turn to the main results reported in this Letter. Using a CF type of scaling (i.e. $T/T_{sp}$ vs. $g\mu_B H/T_{sp}$ where $g = 2.15$ for $H \parallel a$-axis [23]), the scaled PD of CuGeO$_3$ is shown in Fig. 3a for various pressures together with already published data (small squares) [3]. Clearly one reproduces these earlier results quite well at $P = 1$ bar. The transition temperatures and fields used in the scaling are listed in Table I. At low magnetic fields, the D–U transition temperature indeed scales with the square of the field. At higher fields, and in particular for the D-I transition, the scaling no longer holds. Already present at $P = 1$ bar, the problem becomes more acute at higher pressures (Fig. 3a). In order to reconcile the theoretical result with the data, one now has to assume a $T_{sp}$-dependent field scaling factor, which is not very useful if one tries to unify the PD. It seems therefore more appropriate to look for a different kind of scaling law. It is here proposed that $H$ does not scale with $T_{sp}$, but rather with the singlet-triplet gap $\Delta_{ST}$ at zero field. The pressure dependence of $\Delta_{ST}$ has been determined by Nishi et al. [23]: $\Delta_{ST}(P) = \Delta_{ST}(0) + 10.5P$ ($P$ in GPa, $\Delta_{ST}$ in cm$^{-1}$, $\Delta_{ST}(0) = 16.8$ cm$^{-1}$). The resulting scaled PD is shown in Fig. 3b. Clearly the PDs at various pressures now collapse onto each other, despite the observation that the D–I transition occurs before the full closure of the magnetic gap.

In addition to the scaling properties of D–I transition, the scaling of the D-U transition has also improved. The quadratic field dependence found for the D-U transition is:

$$\frac{T_{sp}(H)}{T_{sp}(0)} = \left(1 - 0.384 \cdot \left[\frac{g\mu_B H}{\Delta_{ST}}\right]^2\right)$$

This scaling is not compatible with the CF type of scaling and appears more compatible with the mean field BCS type theory. However, CuGeO$_3$ does not obey this theory since $\Delta_{ST}/T_{sp}$ is not constant as can be inferred from Table 1. As a consequence, one may conclude that the CF theory is not very appropriate to describe the properties of CuGeO$_3$. There are various factors which could explain that, in particular, the presence of a next-nearest neighbor frustrating interaction [23] or the non-adiabacity [25] (the exchange energy is comparable to the phonon energies). It is interesting to see whether the present scaling also applies to organic spin-Peierls compounds such as (TTF)Cu(BDT) [20], (TTF)Au(BDT) [27] and MEM-(TCNQ)$_2$ [28] for which, to our knowledge, $\Delta_{ST}$ has not been directly measured. However, if we speculate for them a value of $\Delta_{ST}/T_{sp} \approx 1.76$ (mean

FIG. 2. a) Variation of $M_0$ at $T = 2$ K as a function of $H$ for different values of the pressure. b) Variation of $M_0$ at $H = 0$ T as a function of $T$ for different values of $P$. c) Variation of $M_0$ at $H = 22$ T as a function of $T$ for different values of $P$. The $M_0$ values have been shifted by 0.0025 for $P = 0.32$ GPa and 0.005 for $P = 0.74$ GPa in b) and c).
field theory), the proposed scaling is surprisingly good for the D–U and even the D–I phase transitions. In particular \( g_H \Delta H / \Delta ST \) ranges between 0.77 and 0.79 for all organic compounds. The surprise comes from the fact that all compounds listed in Table 1 have very distinct properties concerning the existence of frustration, soft phonon modes or variation of \( T_{sp} \) with pressure. This result implies that \( H_c \) does not scale with \( \Delta ST \) as already pointed by Ohta et al. [29].

\[ \Delta ST \]

FIG. 3. Phase diagram of CuGeO\(_3\) for different pressures plotted versus \( T/T_{sp} \); a) scaling of \( H \) with \( T_{sp} \) and b) scaling of \( H \) with \( \Delta ST \). The solid squares are data obtained at 1 bar by magnetostriiction/thermal expansion measurements\(^3\). The dash line represents the variation given by Eq. 2.

In conclusion the study of the ZPL absorption of the intra-center Cu\(^{2+}\) transition has allowed to determine the \( H − T \) phase diagram of CuGeO\(_3\) for different pressures. It has been shown that a Cross-Fischer type of scaling of these phase diagrams is not appropriate. It is noted that a scaling which does not assume a constant ratio between \( \Delta ST \) and \( T_{sp} \) could be more effective, although it relies on two independent parameters \( \Delta ST \) and \( T_{sp} \). We have at present no strong arguments which could support these findings but we hope that this observation will motivate further theoretical research on this special class of compounds.

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TABLE I. Measured phase diagram parameters

| Compound          | P (GPa) | \( T_{sp} \) (K) | \( \Delta ST \) (cm\(^{-1}\)) | \( H_c \) (T) |
|-------------------|---------|-----------------|-------------------------|----------|
| CuGeO\(_3\)      | 0       | 14.2            | 16.8                    | 12.9     |
|                  | 0.32    | 15.5            | 20.3                    | 15.1     |
|                  | 0.74    | 17.0            | 24.7                    | 18.8     |
| MEM-(TNCQ)\(_2\) | 0       | 18              | ?                       | 19.2     |
| (TTF)CuS\(_4\)(CF\(_3\)\(_2\))\(_4\) | 0       | 11              | ?                       | 11.6     |
| (TTF)AuS\(_4\)(CF\(_3\)\(_2\))\(_4\) | 2.0     | ?               | ?                       | 2.1      |