to $T^{3/2}$. Moreover, as can be seen by comparing (21) and (22), the $T^{5/2}$ term in $\langle\mathcal{H}\rangle_{\text{RPA}}$ has only half the expected magnitude. The origin of these discrepancies is not hard to find.

The transverse terms in the Heisenberg Hamiltonian represent the kinetic energy of the magnons and the spin deviations, and they vanish at zero temperature. The longitudinal terms represent potential energy of the spins due to their alignment. As a magnet is heated, spin deviations are produced which increase the magnitude of the transverse terms not only directly, but also indirectly through demagnetization and consequent conversion of the potential energy of the spin alignment to additional kinetic energy. In the case of cubic systems, this is manifested through a cancellation of $T^{3/2}$ terms and an augmentation of $T^{5/2}$ terms in $\langle\mathcal{H}\rangle$. Thus the specific heat depends only on $T^{3/2}$ to lowest order in T. The RPA, however, violates the balance between the transverse and longitudinal terms assumed in deriving (13) and (14), and so spurious terms appear in $\langle\mathcal{H}\rangle_{\text{RPA}}$ which would result in the unphysical prediction of a $T^{1/2}$ term in the specific heat. It is interesting to note that although the replacement in the RPA of $\langle S_{jz}S_{kz}\rangle$ by $\langle S_z\rangle^2$ of itself further violates the internal symmetry, it restores the balance between the transverse and longitudinal terms at low temperatures and patches the spurious result of (21).

If the exact relations (13) or (14) are to be of use in the application of improved approximations, it will be necessary to develop *a priori* criteria for the validity of the results, criteria such as those established by Baym[13] or by Kadanoff and Baym[14] for systems of many fermions.

I would like to thank Dr. R. P. Kenan and Dr. J. F. Cooke for discussion of the problems considered here.

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MOLECULAR DYNAMICS OF ELECTRIC DIPOLES ON A RIGID LATTICE: THE DIELECTRIC RESPONSE FUNCTION

A. Bellemans, M. Gancberg, and M. Köhler
Faculty of Sciences, University of Brussels, Brussels, Belgium

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Dielectric relaxation phenomena are related to the anisotropy of the intermolecular potential and should in principle provide valuable information in this respect. In the present situation of the statistical mechanics of irreversible processes, however, the theoretical calculation of the dielectric response function remains very difficult, even for simple molecular models. We therefore have thought that the method of *molecular dynamics*, which was successfully applied to the velocity-autocorrelation function of gases and liquids,[1] might also be a valuable tool for studying the dielectric response function. This note gives an account of some preliminary results.

To simplify the problem we considered a two-dimensional circular array of 421 molecules (rotators) located on the sites of a rigid square lattice; each rotator has a permanent dipole moment and interacts with its neighbors through an angle-dependent potential. The dielectric response function is defined as

$$\varphi(t) = \langle \vec{M}(t+s)\cdot\dot{\vec{M}}(s)\rangle / \langle \vec{M}(s)^2\rangle,$$

where $\vec{M}(t)$ is the electric moment of the sys-

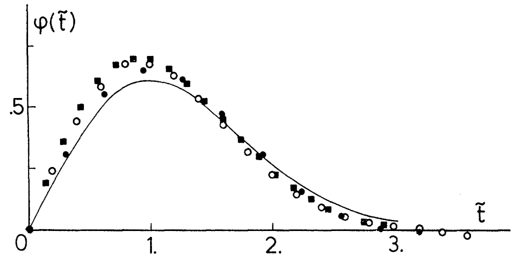

FIG. 1. Response function $\varphi(\tilde{t})$ for the dipolar interaction (2), for various ratios of potential and kinetic energies: −0.26 (●), −0.40 (○), and −1.00 (■). The plain line shows the free rotator response function (1).

tem at time t, and the angular brackets denote a time average. For infinitely weakly coupled rotators, with a nevertheless Maxwellian distribution of angular momenta, one finds

$$\varphi(\tilde{t}) = \tilde{t}\exp(-\tfrac{1}{2}\tilde{t}^2), \tag{1}$$

where $\tilde{t}$ is a reduced time, with the mean period of rotation of a molecule as unity. When a finite coupling is allowed, one expects $\varphi(\tilde{t})$ to differ from (1) and perhaps to approach the Debye function $\tau^{-1}\exp(-\tilde{t}/\tau)$ for $\tilde{t} \gg 1$, where τ is a relaxation time depending on the interactions.

A first series of calculations were made, assuming a strictly dipolar interaction between nearest-neighboring rotators[2]

$$-v\cos(\varphi_i + \varphi_j) \quad (v > 0), \tag{2}$$

where φ_i, φ_j give the instantaneous orientations of dipoles i, j with respect to the i-j lattice vector.[3] The equations of motion were integrated numerically on an IBM 7040 by the Runge-Kutta method, over a time interval much larger than the mean period of rotation of a molecule; $\varphi(\tilde{t})$ was subsequently derived.[4] Three couplings were considered, corresponding to ratios of potential and kinetic energies −0.26, −0.40, and −1.00, respectively. The results are shown in Fig. 1 and compared with the response function (1) for free rotators. Obviously the effect of the dipolar interactions is always very small. The essential conclusion follows that purely dipolar interactions play practically no role in dielectric relaxation and do not lead to the exponentially decaying response function of Debye. (This was anticipated by Zwanzig on the basis of semimacroscopic arguments.[5])

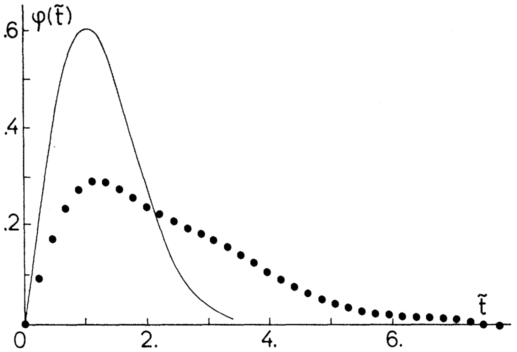

FIG. 2. Response function $\varphi(\tilde{t})$ for the exchange interaction (3), for a ratio −0.25 of potential and kinetic energies. The plain line shows the free rotator response function (1).

Other types of angular potentials exist, which can deeply modify the response function (1) even for weak coupling. As an illustration we considered the nearest-neighbor exchange interaction

$$-v\cos(\varphi_i - \varphi_j) \quad (v > 0) \tag{3}$$

which favors a parallel alignment of the dipoles. The response function for a ratio −0.25 of potential and kinetic energies is shown in Fig. 2. Even though the coupling is weak, the deviation from the response function (1) is large and denotes the appearance of a new characteristic time.

These results show the usefulness of the method of molecular dynamics in the field of dielectric relaxation; further calculations are under way. A theoretical study of the dynamic polarization of the systems considered above has been carried out in the weak-coupling approximation, using the statistical theory of irreversible processes of Prigogine; it agrees substantially with the results reported here.[6]

We thank Professor I. Prigogine and Mr. E. Kestemont for helpful discussions.

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REFLECTIVITY SPECTRA OF $Cd_{1-x}Zn_xS$ SINGLE CRYSTALS

R. E. Drews, E. A. Davis,* and A. G. Leiga
Research Laboratories, Xerox Corporation, Rochester, New York

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The fundamental reflectivity of mixed crystals can provide useful information concerning the electronic band structure of the individual components.[1] The energy at which structure arising from allowed transitions occurs is found to vary continuously with composition, and hence structure corresponding to the same electronic transition can be traced as a function of composition from one constituent to the other. Band-structure calculations rely heavily on the experimental determination of interband separations as deduced from reflectivity measurements. The mixed crystal system $Cd_{1-x}Zn_xS$ is especially important to study because the transition assignments to the various reflectivity peaks in CdS and ZnS are not yet unambiguously identified.

We report here room-temperature reflectivity measurements of hexagonal $Cd_{1-x}Zn_xS$ crystals made between 2 and 5.8 eV with light polarized both parallel ($\mathcal{E} \parallel c$) and perpendicular ($\mathcal{E} \perp c$) to the crystallographic c axis and between 5 and 12 eV for light polarized perpendicular to the c axis. The low-photon-energy reflectance measurements were made at near-normal incidence (4°) using a Leiss prism monochromator. The far-ultraviolet measurements were made with a Tropel vacuum ultraviolet instrument equipped with an S-2 reflectometer.[2] The angle of incidence here was restricted to 20°. A windowless hydrogen discharge served as the light source in the vacuum ultraviolet; tungsten and deuterium lamps were used in the visible and near ultraviolet. The vacuum-ultraviolet-monochromator pumping system was appropriately baffled and trapped to prevent oil contamination of the samples.

The crystals were grown by an iodine-vapor transport technique. The source material was polycrystalline $Cd_{1-x}Zn_xS$ prepared in a flowing-argon open-tube furnace. X-ray studies showed that the crystals were of relatively uniform composition and exhibited hexagonal (wurtzite) structure. Composition was determined to an accuracy of ±1 mole% by a combined x-ray fluorescence and Debye-Scherrer technique.[3] Wherever possible, natural as-grown faces were used for the reflectance measurements. In other cases, oriented faces were prepared by grinding, polishing, and etching.

Figure 1 shows some typical reflectance spectra between 4 and 12 eV for a number of crystals of different composition. These measurements were made on crystals with the c axis perpendicular to the reflecting surface and hence $\mathcal{E}$ was perpendicular to c. The lowest energy reflectance peaks (E_0) have been omit-

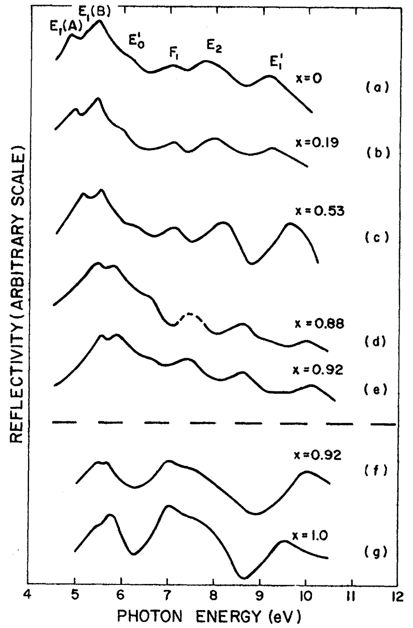

FIG. 1. Typical room-temperature reflectance spectra of several $Cd_{1-x}Zn_xS$ crystals of different composition measured with $\mathcal{E} \perp c$. Curves a-e are for hexagonal crystals, and curves f and g for structurally impure predominantly rotation-twinned cubic crystals.